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Correlation between Physical Properties and Exchangeable Chemistry of Bentonites from the Western United States

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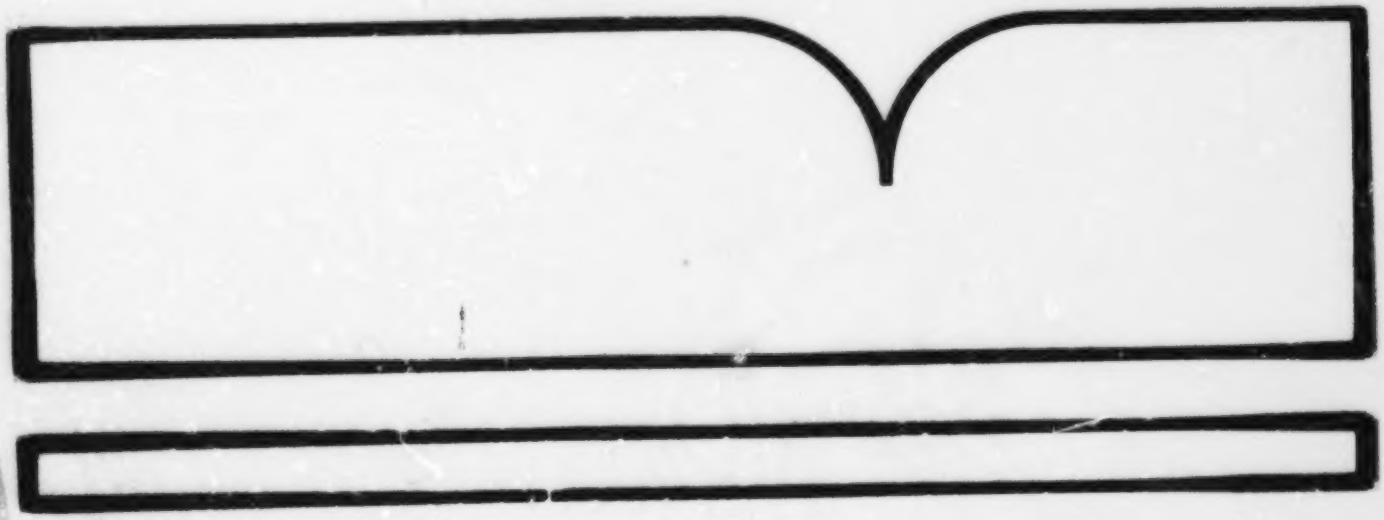

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Certain rheological properties of bentonites from the Western United States vary with changes in the ratio of exchangeable Na/CaMg. Physical properties such as viscosity, water loss and liquid limit are all functions of relative amounts exchangeable sodium, calcium and magnesium ions.

Analysis of over 600 swelling type bentonites from the Western United States suggests that a high grade or exceptional bentonite is one which passes the following properties: viscosity greater than 75-80 bbl/ton, water loss less than 17.0 ml, liquid limit less than 6000%, Na/CaMg greater than o.95, and % of exchangeable Na greater than 48%. Bentonite clays having these properties are reactive to chemical treatment and can be mined and marketable for nearly all of the markets commonly supplied by sweeling bentonite.

It is further proposed that Western United States bentonite be defined according to three well defined varieties: 1) Ca Rich Bentonite 2) Intermediate Ca-Na Bentonite and 3) Na Rich Bentonite. The research reported on in this study also indicates that the blending of bentonites with low yields and high water losses is not feasible with bentonite having properties less than those of a Na rich bentonite.

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U.S. DEPARTMENT OF THE INTERIOR – BUREAU OF LAND MANAGEMENT

CORRELATION BETWEEN PHYSICAL PROPERTIES AND EXCHANGEABLE CHEMISTRY OF BENTONITES FROM THE WESTERN UNITED STATES

by

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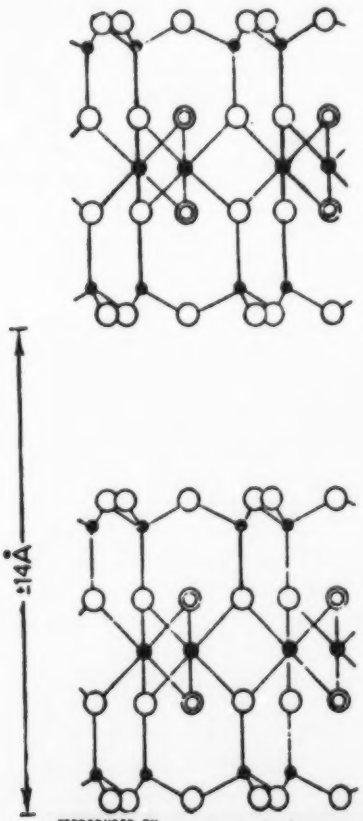

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CORRELATION BETWEEN PHYSICAL PROPERTIES
AND EXCHANGEABLE CHEMISTRY OF BENTONITES
FROM THE WESTERN UNITED STATES

ABSTRACT

Certain rheological properties of bentonites from the Western United States vary with changes in the ratio of exchangeable Na/CaMg. Physical properties such as viscosity, water loss and liquid limit are all functions of relative amounts of exchangeable sodium, calcium and magnesium ions.

Analysis of over 600 swelling type bentonites from the Western United States suggests that a high grade or exceptional bentonite is one which passes the following properties:

Viscosity (yield)	> 75-80 bbl/ton
Water Loss	< 17.0 ml
Liquid Limit	> 600%
Na/CaMg	> 0.95
% Exchangeable Na	> 48%

Bentonite clays having these properties are reactive to chemical treatment and can be mined and marketable for nearly all of the markets commonly supplied by swelling bentonite.

It is further proposed that Western United States bentonite be defined according to three well defined varieties:

1.	Ca Rich Bentonite	Na/CaMg Ratio < 0.1 Exchangeable Na(%) < 5% Yield < 45 bbl/ton Water Loss > 50 ml Liquid Limit < 150%
2.	Intermediate Ca-Na Bentonite	Na/CaMg Ratio = 0.1-0.9 Exchangeable Na(%) = 5%-48% Yield = 45-75 bbl/ton Water Loss = 18 ml-50 ml Liquid Limit = 150%-600%
3.	Na Rich Bentonite	Na/CaMg Ratio > 0.9 Exchangeable Na(%) > 48% Yield > 75 bbl/ton Water Loss < 17.0 ml Liquid Limit > 600%

The research reported on in this study also indicates that the blending of bentonites with low yields and high water losses is not feasible with bentonite having properties less than those of a Na rich bentonite.

I. INTRODUCTION TO THE BENTONITE PROBLEM

The status of bentonite as regards to its disposal under the Mining Law of 1872 has been debated within the Department of the Interior (BLM, USGS and Solicitor) for the past ten years. It has been viewed as a leaseable mineral, a common-variety clay and as a locatable mineral.

Since the late 1960's the Geological Survey has discussed the composition of bentonite as it would apply to the 1920 Mineral Leasing Act. The Solicitor has ruled that based on a report by USGS, bentonite is subject to location under the Mining Law until that statute is amended or the bentonite is made subject to disposal under some other statute (1972). The BLM, through a sequence of Instructional Memorandums has attempted to characterize locatable bentonite using various criteria and standards (1973, 1974, 1977).

At present, the Geological Survey maintains the position that all bentonite deposits are locatable until further guidelines or changes are made in the applicable legislation (1977).

BLM Instruction Memorandums issued over the past several years have provided the necessary guidelines used in investigating the validity of bentonite mining claims. There has been, however, a difference of opinion as to what constitutes a deposit of bentonite that is clearly "of exceptional nature", or high-grade, and thus subject to location. Various attempts were made to define the physical and chemical properties which would make a bentonite deposit exceptional when compared with other deposits. Up to issuance of IM 77-226 (1977), the main physical and chemical criteria used by BLM to designate a bentonite of this caliber have been the API Specifications (1974) outlined in IM 74-343 (1974). These standards cite numerical requirements for viscosity, grit, water loss and pH and are based on a finished product for use as drilling muds. Most bentonite suitable for drilling muds is mined primarily in Wyoming and accounts for about 23% of the total U.S. bentonite tonnage, (Versar Report, 1976). Two other uses of bentonite, foundry and taconite, account for 29% and 31% respectively, thus these three uses make up 83% of the total bentonite mined. In addition, according to the Versar Report (Sargent, Boyer, & Johnson, 1976), 86% of all bentonite mined in the U.S. is Western bentonite.

The intent of this report is to show that a high grade Western bentonite is one which possesses unique properties which can be mined, processed and marketed for all of the major uses. It can

also be sold to most, if not all, of the minor markets existing for bentonite today. It is known that the desirable physical properties which characterize high-grade bentonite are due to a combination of chemical and colloidal properties. Criteria, based on the correlation of the chemical, colloidal and physical properties of naturally occurring bentonite in place, should be the basis for defining high grade bentonite. All of the specifications for drilling mud, taconite and foundry bentonite are based on these properties. Last, but not least, the criteria must be simple and within the capabilities of any bentonite testing laboratory.

Prior Studies

The BLM recognized the need for understanding the chemical behavior of bentonite in 1975, and under the direction of Dr. Claudia Wolfbauer of the USGS, began to select samples of Wyoming bentonite for chemical analysis. The initial intent was to obtain sodium (Na) to calcium (Ca) ratios of bentonite in an attempt to correlate physical properties of bentonites with their chemical compositions and to compare the chemical and physical properties with the geological occurrence of the bentonite. A total of 347 samples were selected by Wolfbauer from bentonite collected during the Wyoming resource study, and from samples collected in Montana and various mineral examination studies on active bentonite proeprties. All of the samples represented Cretaceous age bentonite, 326 samples from Wyoming and 21 from Montana.

All of the samples collected for chemical analysis were analyzed at the BLM bentonite lab in Worland, Wyoming, for the following properties:

Apparent Viscosity
Water Loss
Grit
pH
Plastic Viscosity
Yield Point
Green Strength
Dry Strength

Chemical analysis obtained on these samples consisted of:

1. Water soluble salts - Sodium (Na), Calcium (Ca), Magnesium (Mg), Potassium (K) and Sulfate, (meq/100 gm)

2. Total cation exchange capacity, (meq/100 gm)

3. Exchangeable cations - Sodium (Na), Potassium (K), Magnesium (Mg), and Calcium (Ca), (meq/100 gm)

Attempts to correlate these chemical and physical properties were made independently by the author and Dr. Wolfbauer. Both used different approaches in their work. Regis reported on his work in a preliminary BLM Mineral Report (1976) titled "Correlation of Chemistry with Selected Properties of Wyoming Bentonite - A Basis for Proposed Criteria". Wolfbauer reported on her study in USGS Open File Report 77-158 (1977), titled "Exchangeable Cations in Cretaceous Bentonites from Wyoming and Montana".

Regis defined a high-grade bentonite as one occurring naturally in place and having a minimum yield (apparent viscosity) of 80 bbl/ton and a water loss of 17.0 ml or less. Wolfbauer, in her report, reached the following conclusions:

> "Based on my interpretation of the data plots, the following values are presented as guidelines for depicting exceptional bentonites:"
>
> Apparent Viscosity - > 10-15 (81-90 bbl/ton)
>
> Water Loss - < 15-17 ml
>
> pH - > 8
>
> Swelling Capacity - > 18-20 ml
>
> Water Soluble Cations - 30-180 meq
>
> Exchangeable Sodium - > 20 meq

Current Study

The purpose of this report is to achieve the following:

1. To present a detailed, expanded explanation of the basis for the criteria used in BLM IM 77-226, Part VIII-B-Physical-Chemical Properties for the Deposits. These criteria are derived solely from the correlation of the chemical properties of bentonite with corresponding physical properties such as viscosity (Yield), water loss, analysis of scientific data high grade bentonite and, therefore, bentonite of exceptional nature when compared with other deposits, (2) reflect the characteristics of bentonite in place upon a mining claim as opposed to processed bentonite (3) apply to all bentonite deposits

in the Western U. S. and (4) can be technically defended in any contest actions regarding the locatability of bentonite.

2. To report on further research conducted since the original studies. In the author's first paper, conclusions were based on only 248 samples, all from Wyoming. In this study, samples, representing not only Cretaceous bentonite from Wyoming and Montana, but also Tertiary bentonite from Oregon, California and Nevada.

II. TECHNOLOGY OF BENTONITE

A. Nomenclature

One of the most confusing aspects of the bentonite problem is terminology. There are two basic definitions of bentonite. One is a geologic definition proposed by Ross and Shannon (1926) as follows:

> "Bentonite is a rock composed essentially of a crystalline clay-like mineral formed by devitrification and the accompanying chemical alteration of glassy igneous material, usually a tuff or volcanic ash; and it often contains variable proportions of accessory crystal grains that were originally phenocrysts in the volcanic glass."

The second definition is comparatively new, and is proposed by Grim and Güven (1977). It can be considered as a mineralogical definition and is as follows:

> "...a clay composed essentially and dominantly of a smectite clay mineral, and whose physical properties (plasticity, drilling mud yield, water holding capacity, etc.) are a consequence of the smectite composition".

Most Western bentonites fit both definitions cited above.

Shown in Table 1 are the types of montmorillonite (smectite) and other clay minerals commonly found in the bentonite deposits occurring on public lands.

Sepiolite is included in the Table because it competes with bentonite in the market place and it commonly occurs with Tertiary age bentonite in California and Nevada.

Probably, montmorillonite is the best generic term for the layered clays, but it is "bentonite" that has become the most popular. The term "fullers earth" was once common for Ca montmorillonite or bentonite, but today it appears to be losing popularity in favor of Ca bentonite.

Regardless of the confusion in nomenclature, the real value of all of these clay minerals lies in their physical properties. When the industry sells bentonite, it is really selling some property of the clay which makes it valuable for a particular commercial application.

Table 1. Bentonite and Related Clay Minerals

Clay Mineral Group	Main Minerals	Chemical Composition	Structure	Common Names
Smectites	Montmorillonite	$Ca_{\uparrow}0.33$ $(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$ $\downarrow Na\ 0.33$	Layered	Calcium Form: Fullers Earth, Ca Bentonite, Southern Bentonite, Non-Swelling Bentonite, Sub-Bentonite Sodium Form: Wyoming Bentonite, Na Bentonite, Western Bentonite, Swelling Bentonite
	Hectorite	$Ca\ 0.33 \uparrow$ $(Mg_{2.67}Li_{0.33})\ Si_4O_{10}(OH)_2$ $\downarrow Na\ 0.33$	Layered	Li Bentonite, Hectorite, Li Montmorillonite
	Saponite	$Mg_3(Al_{0.33}Si_{3.67})O_{10}(OH)_2$	Layered	Mg Montmorillonite, Mg Bentonite
Attapulgite	Sepiolite	$Si_8O_{20}Mg_5(OH)_2(OH_2)_4 \cdot 4H_2O$	Fibrous (Amphibole)	Sepiolite, Meerschaum

B. Geology

The geological processes involved in the formation of bentonites are not completely understood. But, basically, bentonite is derived from the alteration or devitrification of glassy volcanic ash under special physical and chemical conditions. Montmorillonite can also result from hydrothermal alteration of either existing clay minerals or volcanic rock. The hectorite deposits in California and Nevada are generally regarded as hydrothermal in origin.

Bentonite deposits in the Western U.S. are of two distinct geological ages. The Cretaceous deposits of Wyoming, Montana, and South Dakota probably were formed in shallow seas, by diagenetic alteration of volcanic ash. The Tertiary deposits commonly found in widespread areas in Oregon, California, Nevada, etc., represent ash falls in shallow alkaline lakes. The John Day Formation in Central Oregon is typical of a widespread occurrence of Tertiary bentonite. Figure 1 is a map showing the more important bentonite deposits in the Western U.S. Nearly all of the deposits shown, outside of Montana, Wyoming, and South Dakota, are Tertiary in age.

Generally, the Tertiary bentonites are "lower grade" in that they contain high amounts of impurities, but one cannot say that all Tertiary bentonites are Ca and all Wyoming and Montana bentonites are Na. The author has found Na bentonites in all of the Western states, but generally in less pure and smaller deposits. Both Tertiary and Cretaceous bentonites occur in layers or lenses usually interbedded with shales and sandstones. The deposits can be irregular in shape and size and easily traced on out-crops.

Much has been written on the geology of the Cretaceous bentonites and the reader is referred to the papers by Knechtel and Patterson (1956, 1962), and Slaughter and Earley (1965). Literature on Tertiary age bentonite deposits is lacking, primarily because these deposits have never been as commercially valuable as the Cretaceous deposits. The largest single use today of Tertiary bentonite is probably for cat litter and pond sealants. A summary of the Tertiary bentonite occurrences in the John Day Formation in Central Oregon is given by Regis (1977).

C. Mineralogy

Bentonites are essentially monominerallic rocks, composed mainly of montmorillonite. The composition of the montmorillonite is highly variable as shown in Table 1, thus affecting the composition of bentonite. This is evident in the different colors of bentonite

Figure 1. Active and Known Bentonite Deposits in Western United States.

rock. The colors can vary even within a working face. Shades ranging from grayish-white, bright yellow, ochre to reddish brown, green and all shades of light and dark blue are common. These colors depend primarily on the iron oxide content of the montmorillonite and the valance state of the iron ions. Minor changes in color are due to varying amounts of iron oxide and organic constituents. Blue bentonite, which is usually deeply buried, contains bivalent Fe^{++} in the montmorillonite structure, whereas yellow, greenish and brownish bentonites contain the oxidized trivalent Fe^{+++} ion.

Another variable in the composition of bentonite is the mineral impurities. Cretaceous bentonites commonly contain 5-10% mineral impurities. Most common are quartz, cristobalite, chlorite, biotite and feldspar minerals. Less common is gypsum, calcite, mica and zeolites. Tertiary bentonites on the other hand, generally contain more mineral impurities. Samples from Oregon, California, Nevada, Idaho, etc., commonly contain zeolites, unaltered ash, tridymite, cristobalite, quartz, K-feldspar minerals, sepiolite, gypsum and calcite (Regis 1977).

The specific gravity of bentonite is variable, but generally is from 2.1 to 2.5. Perhaps the most important property of bentonite is its dispersion behavior in water. When dispersed in water, swelling bentonite will separate into extremely fine particles as follows:

95 to 97% finer than 44 microns (-325 mesh)

90 to 95% finer than 5 microns

70 to 90% finer than 0.5 microns

60 to 65% finer than 0.1 microns

As we will see later, the dispersion properties of bentonite, together with the chemical properties are probably the most important characteristics which give bentonite its commercial uses.

The classification of the various types of bentonite is based primarily on the contents of the exchangeable ions in the montmorillonite structure. Sodium and calcium bentonites are both characterized by high ratios of these respective ions. Intermediate type bentonites can have either ion dominant but in low or equal ratios. All of this can be better explained by looking at the crystal structure of montmorillonite.

The basic montmorillonite structure is often compared to a three layered sandwich - an alumina octahedral layer sandwiched between two silica tetrahedral layers. The octahedral and tetrahedral sheets (layers) are held tightly together by chemical bonds. In a typical montmorillonite crystal, these three layered sandwiches are stacked on top of one another for an infinite thickness. Each of these individual three layered sandwiches are linked to one another by weak Van der Waal forces between the tetrahedral sheets. This is generally the place where cleavage occurs. More important, this is the plane which separates or expands to produce the swelling characteristics when bentonite is dispersed in water. Figure 2 shows a typical montmorillonite crystal structure illustrating the features discussed so far.

Unfortunately, montmorillonites never conform to the theoretical structure just described. There is also a substitution of ions that occurs in all layers of the structure. For example, aluminum commonly replaces some of the silicon in the tetrahedral layer. More important, and much more common, is the replacement of either part or all of the aluminum ions in the octahedral layer by magnesium, iron and lithium.

Where there is substitution of a divalent ion, such as Mg^{++} or Fe^{++}, in the octahedral layer for the trivalent aluminum ion Al^{+++}, a charge deficiency is created. Because of the distance from the charge center to the surface of the structure (interlayer surface), these unsatisfied charges have a very weak bonding attraction. To compensate for these charge deficiencies, the montmorillonite crystal will seize other ions from outside sources, such as Ca^{++}, Mg^{++}, Na^{+}, K^{+}, H^{+} and Li^{+}. These ions are held in the interlayer surface position. Since they are loosely bonded to this surface,they can be easily replaced by other cations, thus they become exchangeable cations. The cation exchange capacity of the bentonite reflects the number of unsatisfied charges in the clay structure. The weak bonding allows water to penetrate the interlayer areas. The type of exchangeable cation in the interlayer sites governs the swelling and cation exchange capacity of the bentonite. The charge, size and concentration of each cation determines which will be dominant. The uni-valent Na^{+} ion is more weakly bonded to the negatively charged silicate surface interlayers than the bi-valent Ca^{++} ion. Therefore, the "energy of hydration" more easily exceeds the weaker Na^{+} ion - H_2O bonds, than the Ca^{++} and silicate layer bonds, allowing adsorption of large amounts of water between the layers. For this reason, Ca bentonites are essentially low swelling, and it is not possible to completely change a Ca bentonite into a Na bentonite by ion exchange because not all of the Ca^{++} can be replaced by Na^{+} ions. This then would imply that below a certain level of Na/Ca ion concentrations, upgrading of low grade bentonite by chemical treatment with sodium compounds would be infeasible. This subject will be fully explored in Parts III to VI of this report.

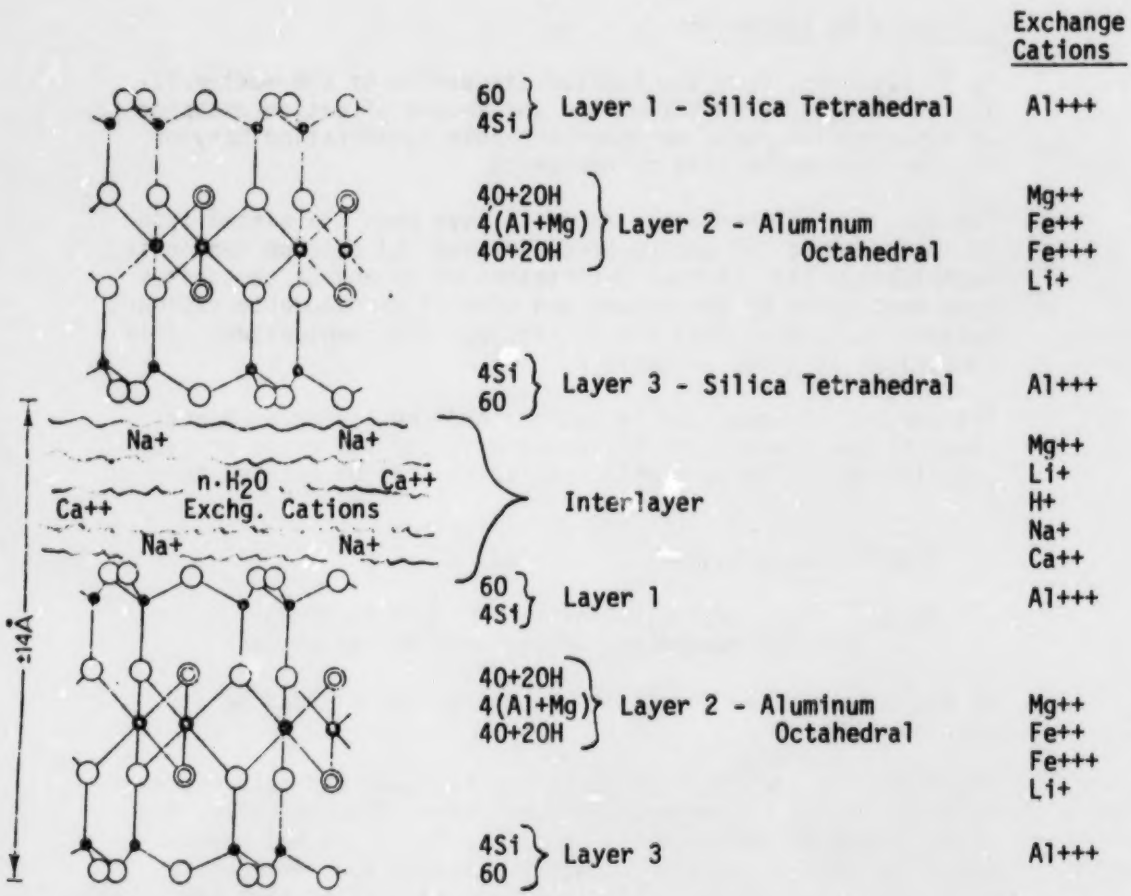
Exchange Cations
60 4Si } Layer 1 - Silica Tetrahedral Al+++
40+20H 4(Al+Mg) 40+20H } Layer 2 - Aluminum Octahedral Mg++ Fe++ Fe+++ Li+
4Si 60 } Layer 3 - Silica Tetrahedral Al+++
Na+ Na+
n·H2O
Ca++ Ca++
Exchg. Cations
Na+ Na+
Interlayer Mg++ Li+ H+ Na+ Ca++
60 4Si } Layer 1 Al+++
40+20H 4(Al+Mg) 40+20H } Layer 2 - Aluminum Octahedral Mg++ Fe++ Fe+++ Li+
4Si 60 } Layer 3 Al+++
≈14Å

Figure 2 Crystal Structure of Montmorillonite. The montmorillonite is shown in the Na bentonite form. The structure extends indefinitely in all directions.

D. Chemistry of Bentonite

It is apparent, from the limited discussion of the montmorillonite structure, that the type and amount of cation exchange or substitution plays an important role in dictating many of the physical properties of bentonite.

For this reason, bentonite deposits have been classified into two major types (a) sodium bentonite and (b) calcium bentonite. Technically, the chemical definitions of Na and Ca bentonites have been given by the amount and kind of exchangeable cations present in Wyoming (Na) and Mississippi (Ca) bentonites. This comparison is given in Table 2.

The amounts of exchangeable cations and the cation exchange capacity are given in milli-equivalents per 100 grams of clay (meq/100 gm). The term milli-equivalent can be equated to:

$$1 \text{ milli-equivalent} = \frac{1 \text{ gram equivalent}}{1000}$$

Thus, 1 milli-equivalent of Na^+ = 0.023 gm of Na^+
1 milli-equivalent of Ca^{++} = 0.020 gm of Ca^{++}

An equivalent of an ion is its atomic weight divided by its valency.

The number of positions at which ion exchange can take place is known as its cation exchange capacity. Theoretically, the total number of exchangeable ions (Na, Ca, K and Mg) should equal the cation exchange capacity. Except for vermiculite, bentonites have higher cation exchange capacities than any other layered clay mineral. Of the 419 bentonite samples analyzed thus far for this study, 80% of them had cation exchange capacities between 40 and 90 meq/100 gm, with the average being about 68 meq/100 gm. Bentonite from Wyoming and Montana had the highest exchange capacities averaging about 69 meq/100 gm. Tertiary bentonites from California, Nevada and Oregon, were slightly lower, averaging about 57 meq/100 gm.

Kaolonite clays, by comparison, only average about 10 meq/100 gm cation exchange capacity.

As seen in Table 2, a Ca bentonite would have a Na/Ca, Mg ratio of only 0.05 and a Na bentonite would have a ratio of 3.0. In reality, few of the 419 samples on which this study is based actually have these ratios. We shall see that the majority of Western U.S. bentonites fall somewhere in between, and that the current definitions of Na bentonite and Ca bentonites are not reflected in most Western bentonites. In fact, as numerous studies have pointed out, a pure Na bentonite has the

Table 2. Comparison of Exchangeable Cations in Wyoming and Mississippi Bentonites (Sanders, 1960)

	Wyoming	Mississippi
Na	65.0 meq/100 gm	0.4 meq/100 gm
K	1.0	2.8
Ca	17.0	64.7
Mg	5.0	1.0
Total	88.0	68.9
Na/Ca Mg ratio	3.0	0.05

same properties as a pure Ca bentonite - both are low swelling and the pure Na variety essentially lacks any desirable properties in its natural state. (Clem and Doehler, 1963; Bleifuss, R. L., 1971, 1973).

The cation exchange properties are of great importance to the physical properties of bentonite, and can be used to predict some of its probable reactions. The ease with which cation exchange can take place and the amount of ions that can be exchanged are also important. This is evident in the common practice today of chemically treating "Ca bentonites". Although a "Ca bentonite" might be treated so that most of the exchangeable calcium ions are replaced with sodium ions, the completeness of that exchange is influenced by structural features of the montmorillonite, particle or crystal size, amounts of impurities and clay content. The physical properties of a natural sodium bentonite cannot be developed in a natural calcium bentonite merely by exchanging Na^+ and Ca^{++} ions, (Smoot, 1962; Clem and Doehler, 1963). The reason for this probably is due to a combination of factors, such as the tighter bonding of the Ca^{++} ions, lower exchange capacity of Ca bentonite and unknown structural features which are inherent to naturally formed Na and Ca bentonites.

In addition to exchangeable cations, bentonites also contain water soluble ions. These ions are Na^+, Ca^{++}, K^+, Mg^{++}, Li^+ and SO_4^{--}. Usually the amount of water soluble ions exceeds the amount of exchangeable ions because of the fixed number of ion exchange positions available in the montmorillonite structure. Wolfbauer (1976) has studied the effects of water soluble ions on the physical behavior of Wyoming bentonite.

Another interesting chemical property of bentonite is the chemical alteration many deposits undergo as a result of near surface weathering. Field relations clearly show that high quality bentonites are the products of such alteration. Bleifuss (1973) has compared this alteration pattern in bentonite to the formation of pedocal soils, which is characterized by calcification in various horizons of a bentonite bed. He goes on to state that near surface bentonite has undergone extensive calcification and in places is so heavily altered as to diminish its swelling properties. Natural high swelling bentonites have undergone only partial calcification. The relatively unaltered "blue" bentonites have undergone little or no calcification. These "blue" bentonites, according to Bleifuss, have the highest Na to Ca ratios, are non-swelling, and do not respond to soda ash additions.

Bentonite on or near the surface commonly contains gypsum crystals which would indicate that the montmorillonite is Ca saturated.

An explanation for the color changes of bentonite from shades of yellow and green near the surface to blue at depth has been proposed by Williams, et al (1952) and Foster (1953). They both attribute these changes to the oxidation state of iron with an increase in depth of overburden. The change from blue to yellow is due to the oxidation of iron from Fe^{2+} to Fe^{3+}. This oxidation change is commonly accompanied by an increase in yield.

Williams, et al (1952) used an idealized type section of a bentonite bed (see Figure 3) to illustrate the progression of this weathering process. During normal weathering, iron oxide is irreversibly removed near the outcrop as hydrous ferric oxide. Interlayered exchange sites left open by the iron removal can be filled by calcium and sodium. Formation of sulfate ion in this weathered zone together with progressive dehydration toward the outcrop removes calcium from the clay and allows additional sodium in as an exchangeable ion. This explains the occurrence of gypsum crystals at the outcrop surface of many bentonite deposits. It also explains the common practice of many bentonite mining companies that uncover a bentonite bed, then rip it into broken aggregates and allow it to weather to enhance its physical properties. Also, many companies will weather bentonite by stockpiling. Sargent, et al (1976, p. 157) reported that this weathering and aging process will change the viscosity of a clay from 85 to 90 bbl.

Occasionally, the hydrous ferric oxide occurring near the outcrops may exert a blocking effect on a portion of the exchange sites in the clay. This can result in a decrease in the cation exchange capacity and a low exchangeable Na content compared to other cations, but with still an increase in yield.

Foster (1953) explains the structural relationship of iron in montmorillonite. In blue bentonite, Fe^{+2} occurs in the octahedral position, substituting for Al^{+3}. As the clay is weathered, oxidization of the iron goes through intermediate states to Fe^{+3}. In typical yellow-green bentonite, nearly two-thirds of the total iron content is present as Fe^{+3}. According to Foster, Fe^{+2} in the octahedral layer causes a redistribution of the electron field of neighboring ions and thus decreases swelling. When the Fe^{+2} oxidizes to Fe^{+3}, swelling is increased because Fe^{+3} has less of a depressing effect than Fe^{+2} on swelling.

Industry uses bentonite primarily for the physical properties, not its chemical composition. The chemical composition, however, cannot be separated from the physical behavior of bentonite. The chemistry must be considered because changes in physical properties accompany changes in chemical composition.

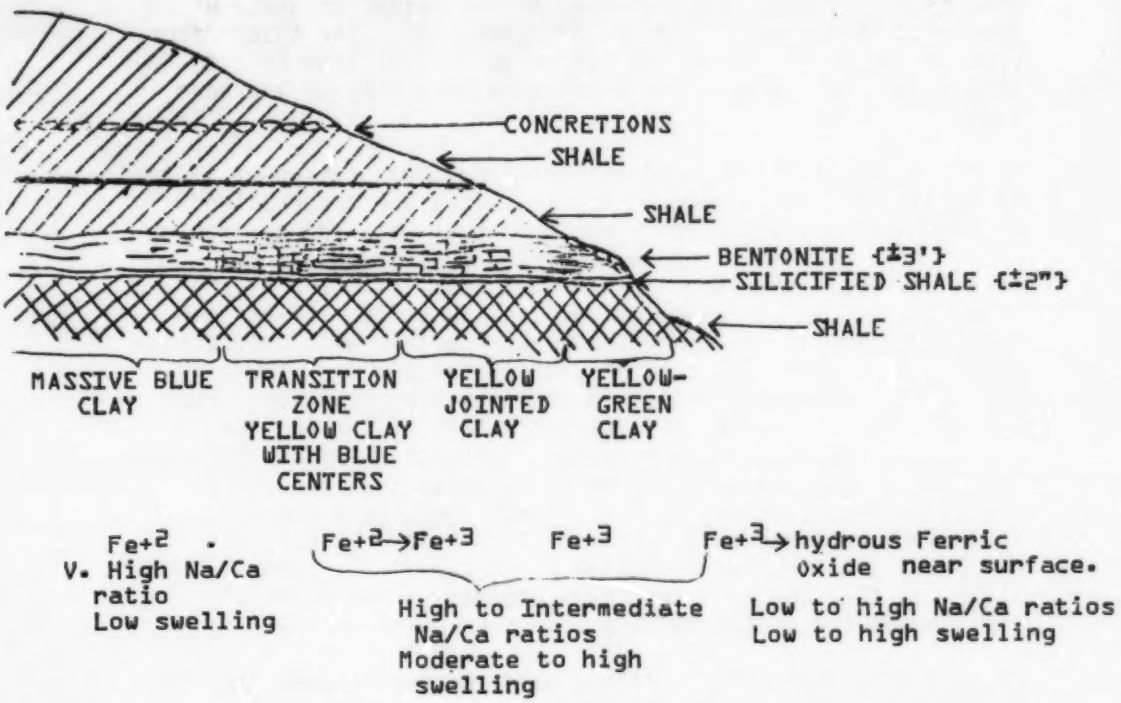

Figure 3 Generalized Cross-Section of a Bentonite Bed Showing Progressive Stages of Alteration. (Modified after Williams, et al., 1952)

E. Physical Properties

1. General Properties - High swelling bentonites, when dispersed in water, will separate into extremely fine particles or flakes. When it is mixed with 7 to 10 parts water, it forms a gelatinous paste; with 15 to 20 parts of water, it forms a milky, flowable solution; in very dilute solutions it will remain in suspension indefinitely. Suspensions of bentonite can form a film or cake over pervious material, acting as a sealant. It can add considerable strength to other materials bonded with it in various concentrations.

Multiple regression analysis of analytical data show that 98% of the variation of yield is due to variation in seven interrelated compositional properties:

1. < 0.2 ν clay content
2. Total clay content
3. Exchangeable Na
4. Exchangeable Ca and Mg
5. Fe^{+2} content
6. Cation exchange capacity
7. Fe^{+3} content

Of these properties, the < 0.2 micron clay content is by far the most important. In other words, the colloidal nature of the bentonite is probably the single most important property. Based upon this statement, one may argue that the chemistry is not as important as previously thought. Studies, however, by numerous investigators on the morphology and composition of particles in size fractionated montmorillonites all find the same conclusions. It is that Na montmorillonite particles tend to separate forming very small, individual unit layers, while Ca montmorillonite particles form large aggregates. The Ca montmorillonite aggregates vary in size and are present throughout the size fractions, while Na montmorillonite particles generally tend to be quite small and occur mainly in the finer fractions. This is primarily due to their tendency to form unit layers. (Smoot, 1962; Wayland, 1971; Sanders, 1960).

As particle size decreases, yield has been found to increase, especially within the < 2 micron fraction. The effect of the < 2 micron fraction upon yield is that yield is calculated from apparent viscosity which is related to the electrochemical energy carried in the crystal structure of Na montmorillonite. This energy imparts swelling, viscosity, gelling strength and other colloidal properties to the clay-water mixture.

One can see from this discussion that the colloidal behavior of bentonite is not solely a physical phenomenon but is also dependent on the chemical composition of the bentonite.

2. Specific Properties - The unique physical characteristics, influenced by subtle but stimulating chemical differences, determine both the classification and commercial applications of bentonite. According to Wayland (1971), slight variations in the Na/Ca ratios profoundly affect the physical properties of a given bentonite.

a. Yield/Viscosity

The capacity to absorb water is the most striking property of Na bentonite. Yield is indicative of the ability of a bentonite clay to build a mud system. Viscosity or yield is quite significant to the proper performance of a drilling fluid. For example, suspension of weight material and removal of formation cuttings is facilitated by maintaining the proper viscosity. The ability of a bentonite to build viscosity with a minimum of solids is important. The yield in barrels per ton is a relative term which has been accepted by the drilling industry as an index to mud building properties. Yield is the number of barrels of 15 centipoise mud which can be mixed in using one ton (2,000 lbs.) of clay and all the water that is needed. Using such quantities of material for test purposes is out of the question. Therefore, laboratory methods have been devised. The three methods presently in use to determine viscosity employ the Fann Viscosmeter, the Marsh Funnel, and the Stormer Viscosmeter. While the Fann is the most sophisticated and accurate, the others are still used to meet the preferences of bentonite customers.

b. Water Loss

One of the most important properties of a drilling mud is the filtration rate or water loss, which is a measure of the relative amount of water lost to permeable formations and of the amount of mud sheath deposited on the permeable walls of the hole.

The water loss is the number of cubic centimeters of filtrate which will pass through a 9 centimeter Whatman #50 filter paper in 30 minutes under a pressure of 100 lbs. per square inch. The water loss can be measured on any bentonite slurry. Generally, the slurries made up for viscosity measurements are most commonly used. A slurry having a viscosity near 15 centipoises will have the most significance. The water loss is measured with a Fann filter press.

c. Water Holding Capacity (Liquid Limit)

This is the ability of clay to hold water. Sodium bentonites hold water very strongly; calcium bentonites hold water also, but to a much lesser degree.

The water holding capacity of bentonite is an important property in steel foundry uses. The water held by bentonite is driven off by heat from molten metal. Bentonites that hold a lot of water, hold it very strongly, thus they release this water very slowly. This slow release of water causes these bentonites to be affected less by thermal dehydration.

Technically, the water holding capacity is the boundary between the liquid and plastic state. The higher the liquid limit, the less weight of clay that needs to be added to a given amount of water to produce a plastic body. The test for liquid limit has been claimed to be capable of determining the quality of a bentonite in regards to its bonding properties and casting qualities. Generally speaking, the lower the water holding capacity of a bentonite, the greater the tendency toward Ca bentonite (Sanders, 1960).

d. Thixotrophy (Gel Formation)

A common characteristic of a bentonite drilling mud is that of thixotrophy; of gelling when allowed to remain quiet over a period of time. This gelling can be observed in the mud pits, or in any container filled with drilling mud. The gel characteristics of a mud govern the pressure reductions in the withdrawal of drill pipe, the settling of cuttings in the pits, and the degassing of the mud. Gelation can also make it difficult to revive circulation after a fresh bit has been run down the well bore.

e. Plastic Viscosity

Plastic viscosity is that part of flow resistance in a mud caused primarily by the friction between suspended particles and by the viscosity of the continuous fluid phase. For practical purposes, plastic viscosity depends on the concentration of solids present and the size and shapes of these solid particles.

f. Yield Point

Yield point is that part of flow resistance attributed to the attractive forces between the particles. It

may be defined as the minimum stress of which continuous flow takes place. This yield point will be evident in tensile, compression, torsion and shear tests but will vary with the rate or stressing and will depend on the manner of specimen preparation. It is dependent on (1) the surface properties of the solids, (2) the volume concentration of the solids, and (3) the electrical environment (concentration and types of ions present) of the solids.

g. Surface Area, Activity and Adsorptive Properties

These properties are all interrelated and common to high grade Ca bentonites and Na bentonites. High surface area, adsorptive characteristics and surface activities are important in such bentonite uses as catalysts, decolorants, water softening, clarification of water, oils, wines, etc. The adsorptive properties of these bentonites allow them to be used as cat litter adsorbents, organic compound adsorbents, (Smoot, 1962).

h. Bonding Properties

Green and dry compressure strengths are commonly specified by the foundry binding markets. High green strength is needed so that the mold can withstand handling before pouring. High dry compression strengths are required to prevent cutting and erosion during pouring. Bentonites high in calcium content, such as Southern bentonites,generally have high green strengths and low dry strengths while Western or swelling bentonites have high dry strengths. Green and dry strengths are expressed as pounds per square inch (psi).

Testing of bentonite for its specific physical properties and use is hampered by the fact that there are no universally accepted specifications for the major uses. Specific tests for evaluating bentonite for a wide application of uses does not exist.

Of the properties listed above, three, viscosity, water loss and water holding capacity are common specifications to the three major markets of bentonite. As we will see later, viscosity is commonly required either as Fann Viscosmeter readings or Marsh Funnel time for drilling muds and taconite, water loss for drilling muds and water holding capacity for foundry binders.

For these reasons, it is suggested that viscosity, water loss and water holding capacity are probably the most important properties for evaluating high grade or locatable bentonite. In addition, these three properties are greatly influenced by changes in the chemistry of the bentonite.

F. Uses

Bentonite uses are as varied as its composition. Of the 3.3 million tons of bentonite mined in 1974 (U.S. Bureau of Mines, 1974), 82% consisted of "swelling" type clay. The U.S. Bureau of Mines listed some 30 uses of bentonite, but the major markets (drilling muds, taconite pelletizing and foundry sand binder) make up 82% of the total. Listed in Table 3 and 4 are the uses and tonnage sold of swelling and non-swelling bentonites respectively.

1. Industry Specifications for Selected Uses

Specifications for uses by industry of swelling bentonite are highly variable. Many are dependent on the particular technology developed by a particular company. For example, some companies demand specifications concerning viscosity, either apparent viscosity or Marsh funnel, others require only moisture and bonding properties. The specifications listed below represent a compilation from 20 companies representing the various industries. The six uses for which specifications are given represent almost 90% of all the tonnage mined. Listed are only those physical properties concerning swelling bentonites and used for the correlation of the chemical data. These specifications, according to use are:

(a) Drilling Muds (6 companies)

Yield = >76 to >95 bbl/ton
Water loss = <15 ml

Water Holding Capacity = >650% (Industrial Minerals, 1973)

(b) Taconite (18 companies)

Yield = 60-105 bbl/ton; 24-32 sec. Marsh Funnel
Average 89 bbl/ton
Water Loss = <16 ml
Water Holding Capacity = >500% (Industrial Minerals, 1969)

(c) Civil Engineering Uses (3 companies)*

Yield = 80± 5 bbl/ton

Water Loss = <15 ml

Water Holding Capacity = >600%

Table 3. Swelling Bentonite Sold/Used in 1974*

Domestic Uses	Short Tons	% of Swelling Bentonite Used
Pelletizing (Fe ore)	870,464	100%
Drilling Mud	584,508	97%
Foundry Sand Binder	467,660	63%
Animal Feed Binder	129,174	74%
Water Proofing and Sealing	84,888	98%
Miscellaneous Uses	54,348	90%
Medical, Pharmaceutical, Cosmetic, etc.	14,678	99%
Filters, Clarifying, Decolorizing, Animal Oils, Fats, Mineral Oils, Greases, etc.	8,269	9%
Paint	4,915	100%
Building Brick, facing	2,922	100%
Pesticides, etc.	2,328	10%
Gypsum Products	506	100%
Cements, Portland	459	100%
Glazes, glass, enamels	209	100%
Catalysts (Oil Refining)	26	1%
	2,225,354	
Export Uses		
Foundry Sand Binder	215,142	93%
Drilling Mud	152,912	100%
Pelletizing (Fe ore)	112,833	100%
Other	21,017	83%
	301,904	
Grand Total	2,527,258	

* U.S. Bureau of Mines Yearbook; Clays; 1974

Table 4. Non-Swelling Bentonite Sold/Used, 1974*

Domestic Uses	Short Tons	% of Total Non-Swelling Bentonite Used
Foundry Sand Binder	270,395	37%
Filtering, Clarifying and Decolorizing, animal oils, mineral oils, greases	83,535	91%
Vegetable Oils	71,290	100%
Animal Feed Binders	46,532	26%
Miscellaneous Uses	27,060	10%
Pesticides, etc.	21,525	90%
Drilling Mud	15,180	3%
Oil and Grease Absorbents	14,860	100%
Roofing Tile	13,129	100%
Fertilizers	6,490	100%
Pet Absorbent	6,319	100%
Catalysts (Oil Refining)	4,853	99%
Waterproofing and Sealing	1,407	2%
Pottery	307	100%
Medical, Pharmaceutical, Cosmetics	200	1%
Sewer Pipe (Vitrified)	100	100%
	583,182	
Export Uses		
Foundry Sand Binder	16,781	7%
Other	4,458	17%
	21,239	
Grand Total	604,421	

* U.S. Bureau of Mines Yearbook; Clays; 1974

(d) Foundry (10 companies)

Steel Foundry:

Yield = 70-90 bbl/ton
Water Loss = <15 ml
Water Holding Capacity = 600-850%

Gray Iron Foundry:

Yield - no specification
Water Loss - no specification
Water Holding Capacity = minimum 100%
no maximum

(e) Pond Sealing, Reservoir Lining, etc.

Yield - no specification
Water Loss = <30 ml
Water Holding Capacity = Minimum 250%
Prefer >400% (U.S. Dept. Agriculture, 1969)

(f) Animal Feed Binders**

Yield - no specification
Water Loss - no specification
Water Holding Capacity = Minimum 100%

(g) Pet Absorbents (3 companies)

Yield - no specification
Water Loss - no specification
Water Holding Capacity - no specification

In order to obtain some indication of the grade of bentonite being used for cat litter absorbents, the author sampled and obtained apparent viscosity and water loss values on two bentonite deposits currently being mined for cat litter. One,

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* Civil Engineering uses consist of ground water control in construction, wall building, grouting, piling and caisson construction, and shield tunnel digging, in addition to other uses.

** Only real specification is that it is "swelling" bentonite. For example, high swelling and water adsorption capacity of Na bentonite makes them attractive not only as animal feed binders but also as an aid in dietary additives for control of wet droppings in chicken cages. (Quisenberry, 1967).

in Kern County, California furnishes bentonite to X-Cel Minerals, manufacturer of Johnny Cat, the other in Crook County, Oregon is the source of supply for Gritco Industries, who make Clover Patch and Purr Fect brands. The yield on these ranged from 0 to 55 bbl/ton and had a water loss range of 35 ml to > 80 ml.

Examination of over 200 data analysis sheets from the bentonite industry which graded eleven major uses of bentonite on the basis of physical properties produced the following conclusions:

(1) Cut off for water loss value which would indicate bentonite reactive to blending and/or chemical treatment was < 16.0 ml. Any bentonite with a water loss value exceeding 16.0 ml was rated as failing for all the major uses. Overall, the water loss physical property is probably the most important in grading bentonite. Agreement from all companies the author has contacted is that bentonite exceeding 16-17 ml water loss will not respond to treatment in order to meet specifications for major uses.

(2) If water loss is low (< 17 ml) some bentonite yields as low as 65-70 bbl/ton could be reactive to blending and/or chemical treatment. As we will see later, however, bentonite with viscosities in this range (65-70 bbl/ton) average 20 ml water loss.

(3) Bentonite for steel foundry binders requires higher grade clay than for gray iron foundry. Most important property is water holding capacity.

(4) Current BLM criteria of 80 bbl/ton yield and <17.0 ml water loss would make bentonite possessing these values pass all 11 uses with blending and/or chemical treatment.

(5) Animal feed binders and gray iron foundry specifications are the lowest and almost all Na bentonite will pass for these uses. One company graded a bentonite with >35 ml water and a viscosity of <30 bbl/ton as passing specifications for the above two uses.

Advances in new technology concerning the uses of bentonite may alter the current specifications required by the various markets. It is fairly safe to assume that the current specifications pertaining to the major uses will not undergo any major changes for some time.

III. TESTING AND ANALYTICAL PROCEDURES

The analytical methods used for the measurement of cation exchange capacity and exchangeable cations in this study are the same as developed by Wolfbauer (1977). This new method was developed by Wolfbauer of the USGS with the aid of Coors Spectro-Chemical Laboratories, Golden, Colorado. The final procedure developed by Coors was further tested for reproducibility, internal consistency and comparability by submitting 25 duplicate samples to Northwest Analytical Laboratories, Powell, Wyoming. The two laboratories analyzed the samples for 10 chemical properties:

Exchangeable Na, K, Ca, Mg

Soluble Na, K, Ca, Mg, SO_4

Cation Exchange Capacity

Slightly over 80% of the values gave good agreement between the two labs; 12% showed fair agreement and 7% were in poor agreement. Tests concerning reproducibility of results by the same labs were also run, with Coors test results being reproducible within 3%. Northwest Labs failed to satisfactorily reproduce their own analyses.

Of the original 347 samples analyzed, 147 were analyzed by Northwest Analytical Labs, 200 by Coors.

On the accuracy and precision of the method, Wolfbauer (1976) concluded that in light of the 80 percent agreement in the data by the two laboratories, and the reproducibility of results by Coors Spectro-Chemical Lab to within 3%, the analytical procedures used come very close to depicting the true exchangeable cation composition of bentonites.

The chemical analysis reported on in this report consists of 309 of the original analyses. The 38 analyses not included were 17 from Montana from the Bearpaw and Hell Creek Shale Formations which did not represent true commercial bentonite beds, and 20 which were included previously as duplicate analyses. In addition to the 309 analyses, 110 more were made - 30 from Tertiary bentonite deposits in California, Nevada and Oregon, and 80 from commercial bentonite deposits throughout Montana. This makes a grand total of 419 analyses used in this study.

Described below is the analytical procedure of the method developed by the USGS and Coors Spectro-Chemical Lab for the analysis of cation exchange capacity and extractable and exchangeable cations.

Cation Exchange Capacity (CEC)

1. Disperse 0.5 g sample in 25 ml of distilled water in a centrifuge tube with a Vortex mixer. Shake for 10 minutes, centrifuge (4500-7500 g) for 10-20 minutes, decant. Repeat 2 more times on the same sample.

2. Disperse the washed sample in 25 ml of sodium acetate (pH=7) in a centrifuge tube with a Vortex mixer. Shake for 5 minutes, centrifuge (4500-7500 gm) for 10-20 minutes, decant the liquid. Repeat this procedure 3 or more times on the same sample.

3. Wash sample 3 times with 25 ml of 95% ethanol. Disperse, shake, and centrifuge as above.

4. Extract the Na index cation with three 25 ml washes of ammonium acetate (pH=7). Disperse, shake, and centrifuge as above. Decand and save the liquid.

5. Analyze the washes (75 ml) of step no. 3 for Na by atomic absorption.

Extractable Cations

A. Water-soluble salts

1. Disperse 0.5 g sample in 25 ml of distilled water in a centrifuge tube with a Vortex mixer. Shake for 10 minutes, centrifuge (4500-7500 gm) for 10-20 minutes, decant and save the liquid. Repeat 2 more times on the same sample. Save sample for part B below.

2. Analyze the washes of step no. 1 for Na, Ca, Mg, K, by atomic absorption, and So_4 by a wet chemical technique.

B. Exchangeable cations (EC)

1. Disperse the sample from part A-1 above in 25 ml of $BaCl_2$ solution (0.1N $BaCl_2$ in 68% C_2H_5OH) with a Vortex mixer. Shake for 5 minutes, centrifuge for 10-20 minutes, decant and save liquid. Repeat 2 more times.

2. Analyze the liquid for Na, Ca, Mg, and K.

IV. CHEMICAL DATA EVALUATION

A. Statistical Method - Chemical Data

The statistical approach used to evaluate the chemical data is similar to that reported in the following standard texts on statistics: Miller and Freund (1965); Hazen (1967); Bennett and Franklin (1954).

In order to correlate the chemistry and physical properties in a meaningful manner, the analyzed samples were divided into groups based upon their apparent viscosity (yield). These groupings consist of:

	Yield (bbls/ton)	Apparent Viscosity
1.	>110	>30.0
2.	101-110	20.5-29.5
3.	90-100	14.0-20.0
4.	80-89	10.0-13.5
5.	70-79	7.0-9.5
6.	60-69	4.5-6.5
7.	50-59	3.0-4.0
8.	46	2.5
9.	40	2.0
10.	30	<2.0

Using yield as the prime index upon which the statistical groupings are based, statistical treatment of the chemical data as Na/CaMg ratio was attempted within each group.

1. Determination of Average Value - If, within each yield grouping, the plot of the frequency distributions of the Na/CaMg ratios of the exchangeable cations were symmetrical, the arithmetic mean ($\bar{x}$) is the correct average to use. In fact, if the data has a symmetrical distribution, the arithmetic mean ($\bar{x}$), the mode, and the median ($\bar{m}$) would all coincide. This is not the case with the frequency distributions representing the chemical data (Na/CaMg ratios) in this study. All of the frequency distributions within the

yield groupings are assymmetrical or skewed. Because of the assymmetrical distribution of the data, a true average value must be one which is unbiased toward extreme values. The arithmetic mean tends to be unduly biased towards the extreme numbers. The geometric mean (Mg) is the proper average to use when averaging values that are drawn from an assymmetrical distribution or one which follows a geometric progression, i.e., the numbers do not increase or decrease the same amount each grouping.

To simplify the calculation of the geometric mean, the logarithmic form is used for a frequency distribution:

$$\text{Log } \bar{Mg} = \frac{fi \cdot \log (mp)_1 + fi_2 \cdot \log (mp)_2 + \cdots fi_n \cdot \log (mp)_n}{N}$$

or

$$\text{Log } \bar{Mg} = \frac{\Sigma [f(\log mp)]}{N}$$

where f is frequency, mp is the midpoint of an arbitrary group of Na/CaMg values, and N is the total number of values.

The geometric mean is a calculated value and depends on the size or value of all the data. It is always equal to or less than the arithmetic mean because it is less affected by extreme values. In a frequency distribution that approximates a lognormal binomial, the value of the geometric mean will be close to or equal the value of the median. In cases where the frequency distribution is normal or symmetrical, the geometric mean will have the same value as the arithmetic mean.

2. Determination of Variances and Standard Deviation

The standard deviation is the square root of the variance. It is defined as the square root of the mean of the squares about the geometric mean. The standard deviation is designated by the Greek letter sigma (σ) when referring to the standard deviation of the entire population of values from which samples have been selected. The letter S is used to denote the standard deviation of the samlpe, and the value of S is an estimate of σ.

The standard deviation about the geometric mean is:

$$S\bar{g} = \sqrt{\frac{\Sigma(f)(\log mp)^2}{N-1} - \left[\frac{\Sigma(f)(\log mp)}{N-1}\right]^2}$$

Since the standard deviation is affected by the value of each sample analysis, emphasis is placed on the extremes because all values are squared in the calculation. Standard deviation is used in the evaluation of the chemical data in order to measure the fluctuation of the analysis about the geometric mean.

If we assume that the standard deviation of the total sample population is both a fair and unbiased estimate of the true standard deviation, σ, then the standard error of the mean ($S\bar{g}$) can be used to establish the precision of the estimate of the Na/CaMg ratio of each grouping. The standard error of the mean $S\bar{g}$ is equal to:

$$S\bar{g} = \frac{S}{\sqrt{N}}$$

where S is the sample standard deviation of the chemical analysis (Na/CaMg) frequency distribution and N is the number of analyses used in the distribution within each yield grouping. Thus, each yield grouping will have an individual geometric mean ($\bar{M}g$) and standard deviation ($S\bar{g}$) about this mean.

3. Confidence Interval - The confidence interval (CI) can be calculated from the standard error of the geometric mean by the formula:

$$\frac{CI}{2} = S\bar{g}\ (To.o5)$$

where To.o5 is a standard statistical table value (Hazen, 1967) based upon the number of samples (n) and the 95 percent level of confidence (1.0-0.95=0.05). The size of the confidence interval depends upon the number of samples and the standard deviation ($S\bar{g} = \frac{S}{\sqrt{N}}$). The confidence interval establishes limits above and below the estimated geometric mean of the Na/CaMg ratios. The confidence interval can be considered as covering the true average Na/CaMg ratio range of each yield grouping that is

represented by a distribution of Na/CaMg ratios and if the standard deviation estimate of $S\bar{g}$ is a good and unbiased estimate. Shown in Figure 4 is a plot of Na/CaMg values from the yield grouping of 80-89 bbl/ton showing the fluctuation of the values about their geometric mean. The number of values plotted fall within 1S (68%) and 2S (95%) limits. This indicates that the $S\bar{g}$ estimate for this yield grouping and Na/CaMg ratio geometric mean is a good and unbiased estimate. Since the standard deviation is good and unbiased, there is a 95 percent probability that a deviation as great as this could occur by chance alone.

B. Statistical Method - Physical Data

1. Yield (Apparent Viscosity) and Water Loss

For the two properties of yield and water loss, the arithmetic mean ($\bar{x}$) was used since both had normal symmetrical frequence distributions. Water loss values were averaged for each yield grouping.

2. Water Holding Capacity - Over 200 water holding capacity values were grouped according to their apparent viscosities. In all but two yield groups, their value had normal frequency distributions. Where this occurred, arithmetic means ($\bar{x}$) were used to correlate this property with water loss and yield. Two groupings had assymetrical frequencies, and a geometric mean was calculated for their water holding capacities (60-69 and 50-59 yield groups).

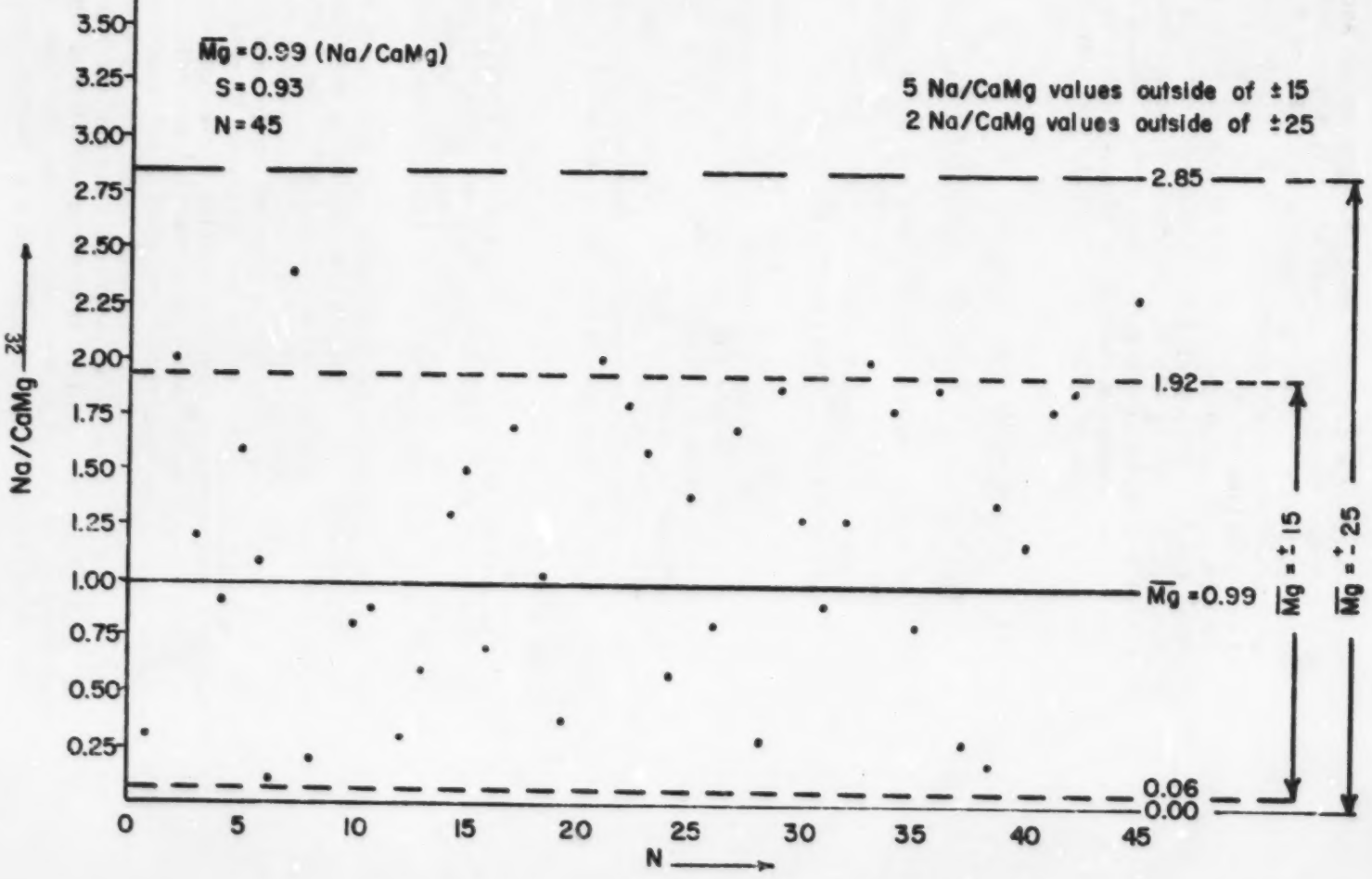
C. Discussion

The statistical approach used in the author's preliminary report was not fully explained. This was primarily because the first report was of a preliminary nature with the sole intent to report its conclusions to the Washington Office.

The samples upon which the statistics are based were selected from those taken during the Wyoming Bentonite Resource Study conducted by the Wyoming State Office, BLM. The findings of this study were reported on by Bestram (1977). According to Bestram, samples were collected from bentonite beds having a thickness of at least 1.5 feet and less than 75 feet of overburden. Any bentonite beds not meeting these requirements were not considered mineable or commercial bentonite and were not sampled. The majority of the samples collected were by channel methods from outcrops, hand auger, and by auger drilling. All samples collected were carefully examined for representation and lack of contamination. Samples not considered representative or found to be contaminated were discarded (Bestram, 1977). Samples collected in Montana, California, Nevada, and Oregon underwent the same scrutiny.

Figure 4. Plot of Na/CaMg Ratios About Their Geometric Mean ($\overline{Mg}$)
For Yield Grouping 80–89 bbl/ton.

*4.5



D. Correlation of Chemical Data with Physical Data

Upon completion of the statistical treatment, the chemical data, expressed as Na/CaMg ratios and percent exchangeable Na were correlated with the physical data by plotting the respective values. Shown in Table 5 is a compilation of the statistical data and selected physical properties. From this table, all of the correlation curves were constructed.

Also shown in this table are average pH, green and dry strengths for each yield grouping. These three properties are averages from the 248 samples reported on in the author's first report. In regards to pH, it is evident that a general correlation occurs between pH, yield and Na/CaMg ratio. From a yield of 65 bbl/ton upward the pH is quite uniform, varying only from 8.8 to 9.1 at a yield of >110 bbl/ton. It can be concluded therefore that pH is not an indication of exceptional bentonite. Correlations between green and dry strengths and chemistry were attempted but as can be seen from Table 5, no correlations exist between these properties. This would indicate that, for Western U.S. bentonite, green and dry strengths are not significantly dependent on the chemistry of bentonite or on physical properties such as water loss, yield or pH.

Table 5. Compilation of Statistical Data and Selected Physical Properties

Yield-$\bar{X}$		No. Samples	Na/CaMg $\overline{Mg}$	CI ±2σ	% Exch. Na	Water Loss $\bar{X}$	Water Holding Cap. $\bar{X}$	No. Samples	pH $\bar{X}$	GS** $\bar{X}$	DS** $\bar{X}$
>110	123	30	2.64	3.44 1.84	73	12.2	--	--	9.1	8.5	164
100-110	105	33	1.66	2.11 1.21	63	13.1	--	--	9.1	9.1	154
90-99	95	42	1.28	1.66 0.90	56	13.8	744	13	9.0	8.6	164
80-89	85	45	0.99	1.29 0.69	50	15.6	620	28	8.8	8.8	155
70-79	76	49	0.94	1.20 0.68	48	17.5	612	30	8.9	7.7	165
60-69	65	52	0.68	0.88 0.51	40	20.5	*495	55	8.8	8.3	155
50-59	55	55	0.34	0.41 0.27	25	28.5	*265	56	8.3		
	46	24	0.22	0.26 0.18	18	51.5	283	13	7.3		
	40	47	0.06	0.07 0.05	5	90.0	--	--	6.7	7.5	157
	30	42	0.04	0.04	3	98.2	130	11	~6.7		
		419						206			

* Water Holding Capacities at 60-69 and 50-59 yield ranges are geometric means.

** GS - Green Strength, psi
DS - Dry Strength, psi

V. DISCUSSION OF RESULTS

The results of this study center around the following seven relationships:

1. Na/CaMg ratio vs Yield
2. $\frac{1}{\text{Na/CaMg}}$ ratio vs Yield
3. Yield vs Water Loss
4. Na/CaMg ratio vs Water Loss
5. Yield vs Water Holding Capacity
6. Na/CaMg ratio vs Water Holding Capacity
7. Water Loss vs Water Holding Capacity

A. Na/CaMg Ratio vs Yield

Figure 5 illustrates the relationship between Na/CaMg ratio and yield. Also shown in this graph is the percent of exchangeable Na at a particular Na/CaMg ratio and yield. This graph represents the role of exchangeable sodium and its effect on the yield.

The most important feature of Figure 5 is the plateau which occurs between 75 and 85 bbl yield. This plateau is indicative of the Na/CaMg ratio at which high grade bentonite begins. Within this range, it is postulated that the bentonite is in an "unstable" exchange state in which a naturally occurring bentonite is highly reactive to chemical treatment. Below this range, or about 75 bbl yield, the influence of Ca^{++} on the bentonite is much more pronounced. Above this range, the influence of Na^{+} upon the swelling characteristics of the montmorillonite is critical. It is suggested, therefore, that bentonite with Na/CaMg ratios at the plateau level and above is high-grade bentonite, or typical Wyoming or Na bentonite. Bentonites below the plateau still may exhibit some swelling properties, but the bentonite will not be as likely to respond to ion exchange treatment. This bentonite, which commonly occurs throughout the Western U.S. is a mixed Ca-Na montmorillonite in which the Na/CaMg ratio is less than 0.9 and will contain greater than 52% of exchangeable Ca and Mg. This is particularly evident when the yield, chemistry and water loss are all considered together.

Is this threshold plateau real? Clem (1976) in a report on high temperature bonding with Wyoming bentonite also found a break in a plot of water holding capacity with yield. According to Clem, "this break, as small as it may be, occurs at the same position as the reported threshold in the 1976 BLM Minerals Report (Regis

Figure 5. Correlation Between Na/Ca Mg Ratio and Yield.

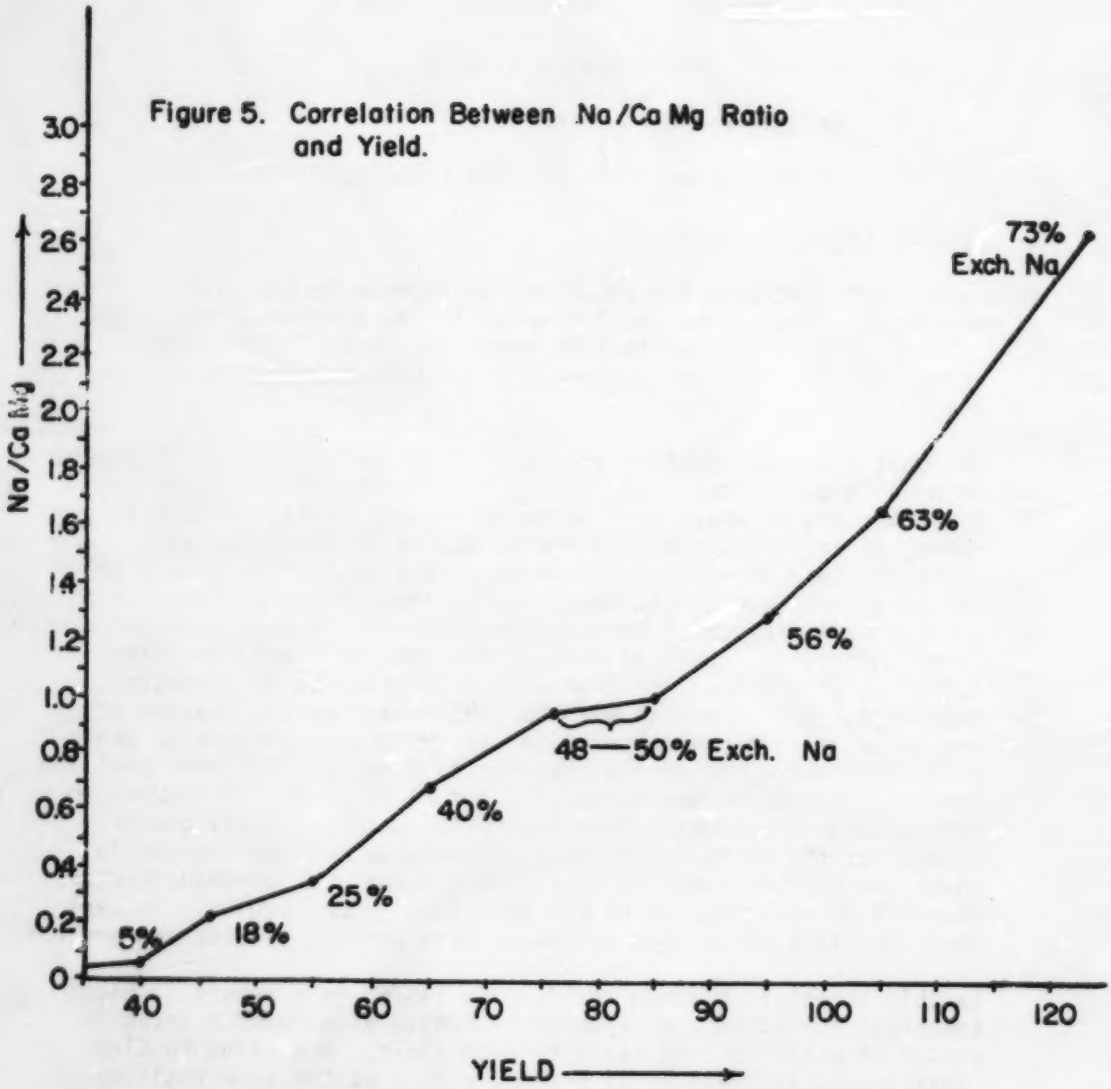


Figure 1)." Clem found his break to occur between 550% and 630% water holding capacity. This is equivalent to a range of approximately 70 to 82 bbl yield (Figure 9) and an exchangeable Na content of 45-51%. The plateau values in this report are within these ranges.

The Steel Founders Society of America (1965) classifies Western bentonite as having a Na/CaMg ratio of 1.0 to 1.7. The plateau in Figure 5 begins at a Na/CaMg ratio of 0.94 and extends to 0.99. This would imply that the Steel Foundry Society's definition of Western bentonite essentially agrees with the one suggested in this study. In addition, the range of 1.0 to 1.7 would correspond to an exchangeable sodium of 49% to 64%.

More significant is the work by Williams, et al, 1953, in which they investigated the effects of exchangeable bases on the colloidal properties of bentonite. Although much of their work was on bentonites which were ion-exchanged (purified) in the laboratory and not on natural untampered samples, as was the case in this study, the conclusions in the two studies are similar. Williams, et al, state that sodium bentonite adsorbed 40% of the base exchange capacity as calcium before a notable decrease in viscosity occurred. Figure 5 indicates a steady decline in viscosity with the addition of exchangeable calcium down to 50%-48% sodium (or 50%-52% calcium). This corresponds to the plateau range shown in Figure 5. According to Williams, bentonite had the greatest range of instability in the 40%-60% exchangeable sodium range. They state that this is the range where additions of either sodium and/or calcium can induce large changes in the rheological properties of bentonite. This study would indicate that this range of instability begins at 48%-50% exchangeable sodium or at a viscosity range of 75 to 85 bbl.

A second plateau occurs in the range of viscosity from 40 bbl and less. This plateau corresponds to an exchangeable sodium content of 5% and less. This area might be considered as the threshold beginning of the calcium end-member of bentonite or true "Ca-bentonite".

B. Reciprocal Correlation of Na/CaMg vs Yield

The influence of exchangeable calcium upon yield is shown in Figure 6. This is evident by the relative slopes of the lines from 50% exchangeable calcium to 27% calcium and from 52% exchangeable calcium to over 82% calcium. The effect of calcium on the viscosity of bentonite is dramatically illustrated from 75 bbl yield down to less than 50 bbl. On the other hand, the effect of calcium on viscosity over 75 bbl is much less pronounced. The effect of calcium on viscosity is minimal from 75

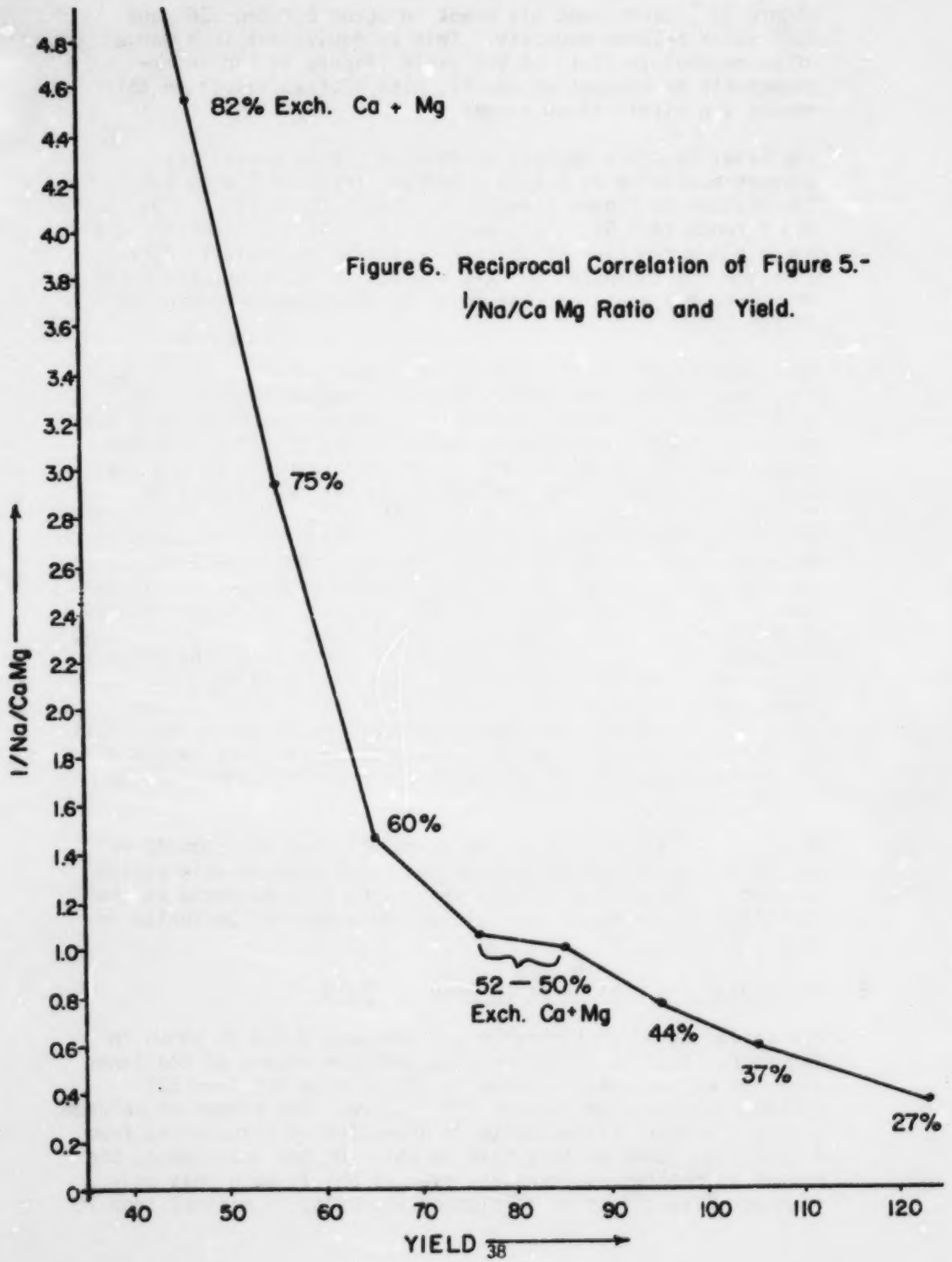


Figure 6. Reciprocal Correlation of Figure 5.- 1/Na/Ca Mg Ratio and Yield.

to 85 bbl and 50-52% calcium. This, again marks the threshold range where bentonite begins to become reactive to treatment.

C. Correlation between Water Loss, Viscosity and Chemistry

Probably the most important property of bentonite is its water loss. This opinion is also shared by Dresser Industries (Bestram, 1977). Williams, et al (1953), recognied the relationship between viscosity and water loss and their dependence on the exchangeable cation types. This study also points out the relationship between these three properties. Figure 7 illustrates the interrelation between water loss and chemistry. The increase in water loss from Na/CaMg ratios 2.64 to 1.0 is only 12.2 to 15.0 ml. The water loss then increases to 17.5 ml as depicted by the gap shown in Figure 7. From this point, water loss dramatically increases as the sodium content decreases. This fluctuation in water loss occurs at the same place where the plateaus shown in Figures 5 and 6 occur. This corresponds to a viscosity range of 75 to 85 bbl. Since the water loss value at the low side of this plateau is 17.5 ml, this would indicate that bentonite with water loss less than this amount would be responsive to treatment. In other words, given a naturally occurring bentonite with a water loss of less than 17 ml and greater than 75 bbl yield, the probability is that this bentonite would be reactive to chemical treatment and blending in order to produce high grade bentonite of oil drilling grade specifications. In addition, such a treated or untreated bentonite could also meet any demands of the taconite and foundry industries. These three markets make up 83% of the bentonite industry. Thus a water loss of less than 17.5 ml is critical. What does industry consider a critical value? In an affidavit by Fulton (1970) of American Colloid, he states that "Our fluid loss standard is 13.5 ml, but we find that anything with a fluid loss of 15.0 or less usually can be treated economically and be brought within the standard." As stated on page 25 of this paper, an examination of over 200 data analysis sheets from a major bentonite company indicated that the cut off for water loss which indicated bentonite reactive to blending and/or chemical treatment was less than 16.0 ml. They rated bentonite with a water loss of over 16.0 ml as failing for the three major uses.

The relationship between water loss and viscosity is shown in Figure 8. A direct correlation can be seen between these two properties with a gradual increase in water loss with a decrease in viscosity to about 65 bbl. Based on the above facts, and using 17.5 ml as a cutoff for water loss, a yield of 75 bbl corresponds to this water loss. Although it is possible that a naturally occurring bentonite with a yield of 65 bbl or more could be treated if it had a water loss of less than 17.5 ml, it is unlikely that such a bentonite would occur in great quantity. Figure 8 shows that the average water loss for a 65 bbl bentonite is over 20 ml.

Figure 7. Correlation Between Na/Ca Mg Ratio and Water Loss.

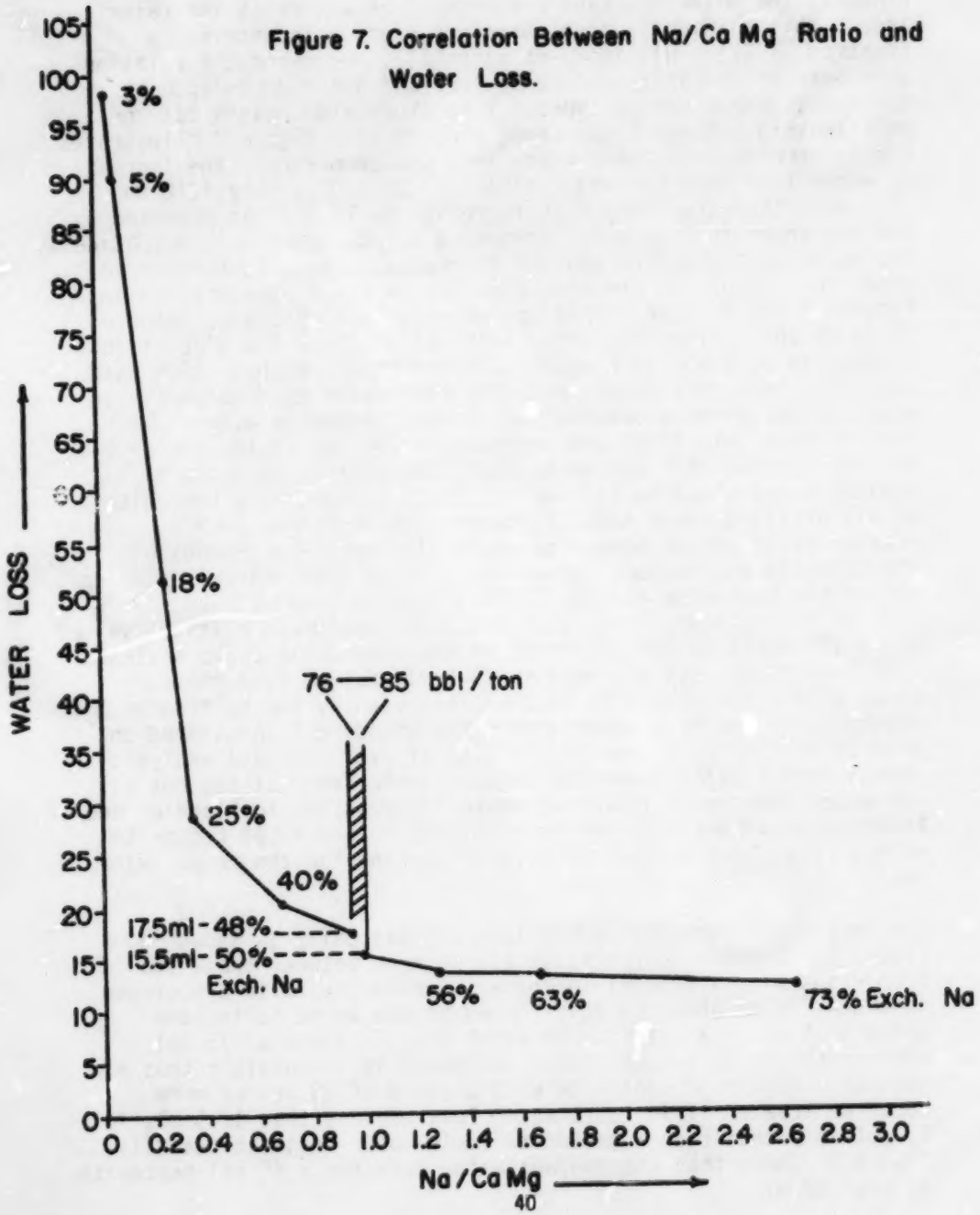
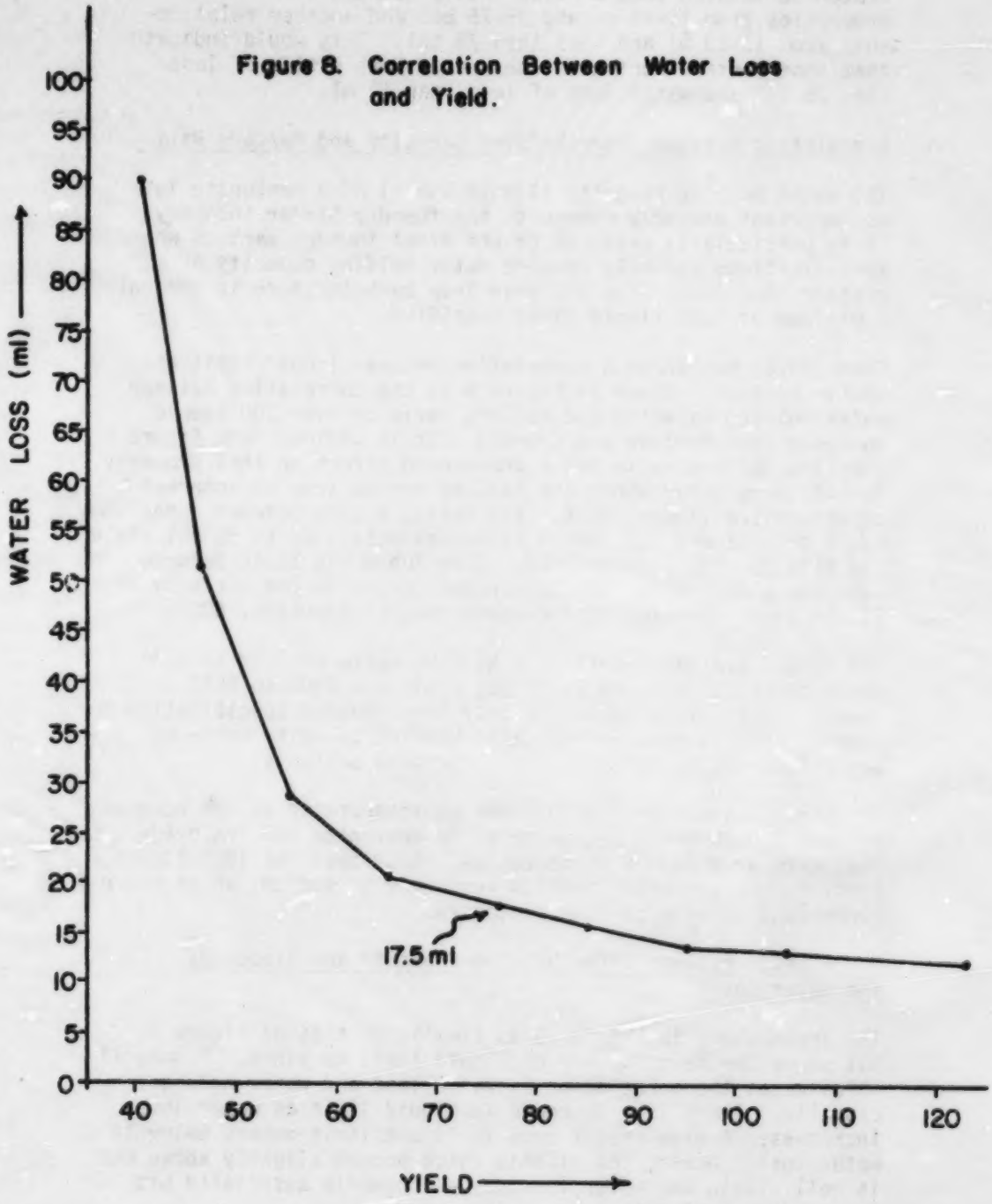


Figure 8. Correlation Between Water Loss and Yield.



Studies carried out by Stuerwald (1977) in Montana on the correlation between water loss and yield on 414 Montana bentonite samples show a relationship between these two properties from 11-15 ml and 95-75 bbl and another relationship from 15-23 ml and less than 75 bbl. This would indicate that some Montana bentonite does occur with yields of less than 75 bbl and water loss of less than 17 ml.

D. Correlation between Water Holding Capacity and Na/CaMg Ratio

The water holding capacity (liquid limit) of a bentonite is an important property common to the foundry binder industry. It is particularly critical to the steel foundry markets where specifications commonly require water holding capacity of greater than 600%. For the gray iron markets there is commonly a minimum of 100% liquid limit specified.

Clem (1976) has shown a correlation between liquid limit and sodium content. Shown in Figure 9 is the correlation between water holding capacity and Na/CaMg ratio on over 200 sample analyses from Montana and Wyoming. It is obvious from Figure 9 that the Na/CaMg ratio has a pronounced effect on this property. Two plateaus occur where the Na/CaMg ratios show no apparent effect on the liquid limit. The first, occurs between a Na/CaMg ratio of 0.83 and 1.0, which is approximately 73 to 85 bbl yield and 612% to 620% liquid limit. Clem found his break between 550% and 630%. Note that this break occurs in the vicinity of liquid limit required by the steel foundry industry, 600%.

The second plateau occurs at a Na/CaMg ratio of 0.22 to 0.38, which corresponds to 46 to 56 bbl yield and 250% to 265% liquid limit. This is in the gray iron foundry specification range. This is also in the water holding capacity range of bentonite meeting specifications for pond sealants.

The first plateau in Figure 9 can be interpreted as the boundary between a high grade bentonite or Na bentonite and low grade bentonite or mixed Ca-Na bentonite. Note that the 100% liquid limit occurs in bentonite with less than 5% sodium, which would correspond to high calcium bentonite.

E. Correlation between Water Holding Capacity and Viscosity and Water Loss

The graph shown in Figure 10 is similar to that of Figure 9, but shows the relationship of liquid limit to yield. Figure 11 illustrates the correlation of water loss and water holding capacity. There is a decrease in liquid limit as water loss increases. A significant drop in liquid limit occurs below 14 ml water loss. Again, the plateau which occurs slightly above 600% is well within the water loss values commonly associated with a true sodium bentonite.

Figure 9. Correlation Between Water Holding Capcity (%) and Na/Ca Mg Ratio.

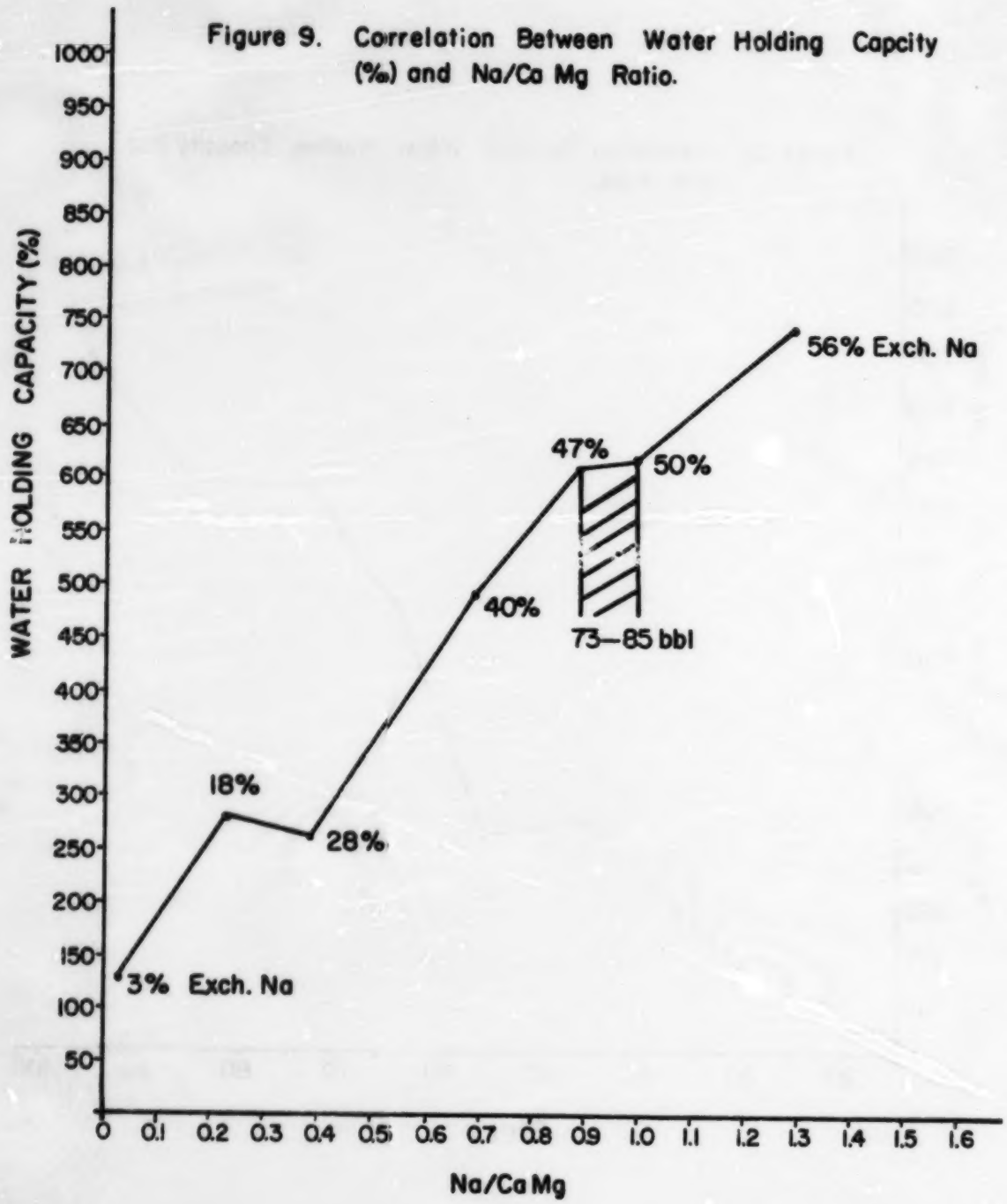


Figure 10. Correlation Between Water Holding Capacity (%) and Yield.

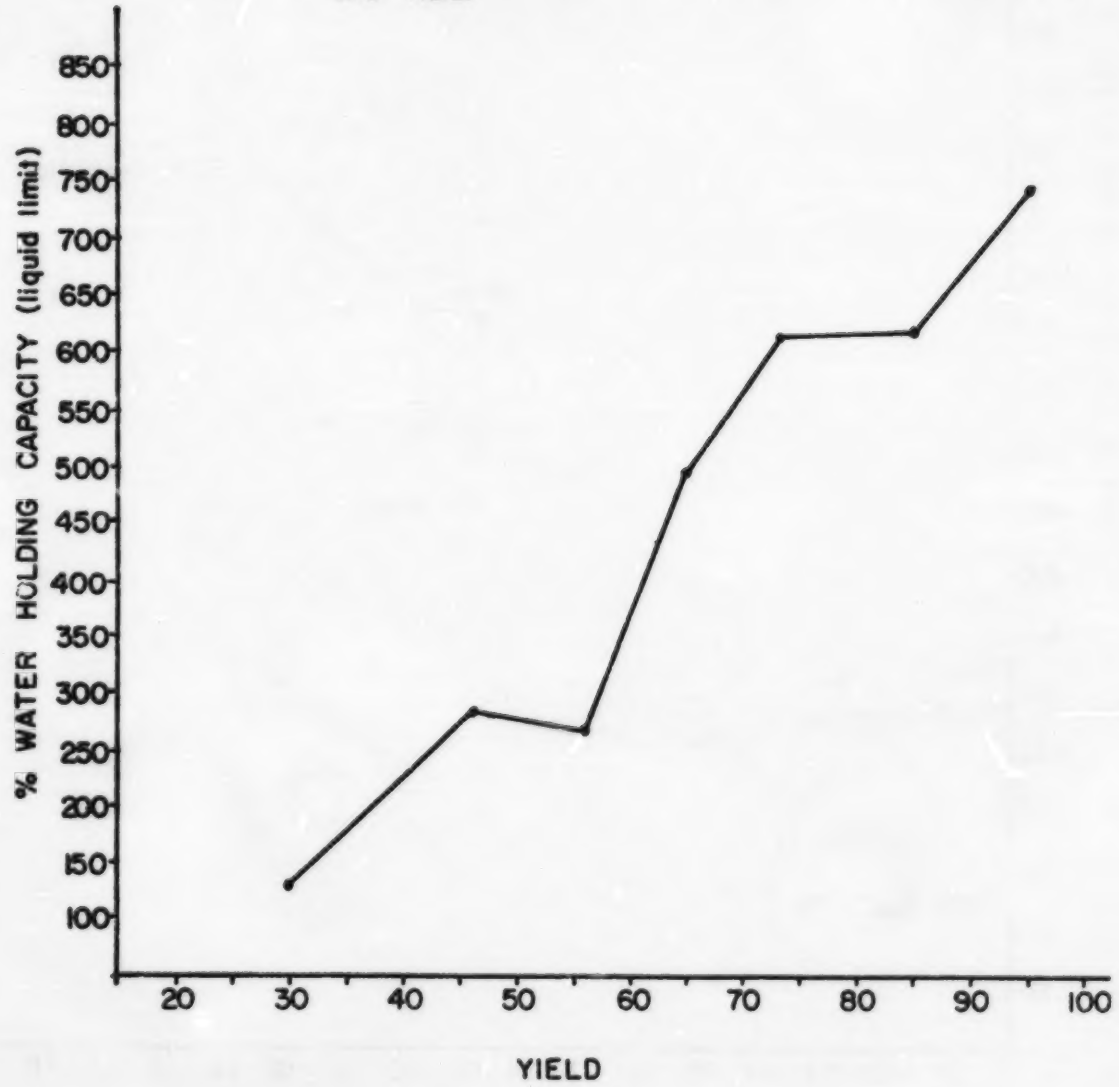
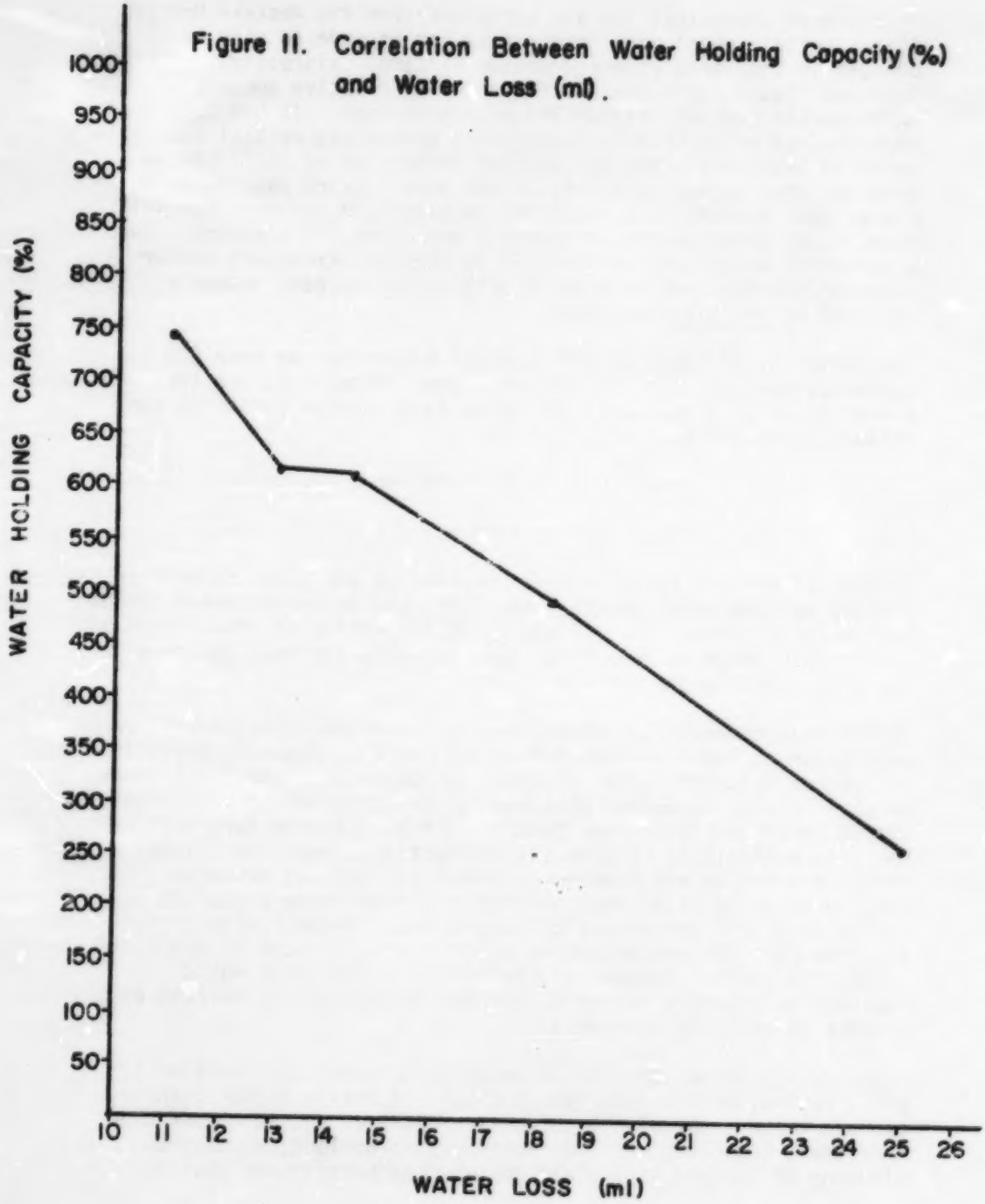


Figure 11. Correlation Between Water Holding Capacity (%) and Water Loss (ml).



VI. CONCLUSIONS

It has been shown that for any bentonite from the Western United States certain rheological properties can be made to vary by changes in the ratio of exchangeable Na/CaMg. Viscosity, water loss and liquid limit are all functions of relative amounts of exchangeable sodium, calcium and magnesium ions. It has long been debated as to what is exceptional bentonite, or that bentonite which is locatable under the General Mining Law of 1872. It is proposed that such a bentonite is one which occurs naturally, in place, upon a mining claim and can be mined and marketed for all three major markets without chemical treatment and blending. Such a bentonite would also be reactive to chemical treatment and/or blending and thus can be made to satisfy all markets commonly supplied by swelling bentonite.

Investigation of chemical and physical properties on over 600 bentonite samples from the Western United States suggests that a high grade or exceptional bentonite is one which possesses the following properties:

Yield	> 75-80 bbl/ton
Water Loss	< 17.0 ml

Bentonites meeting these physical properties are shown to have an average Na/CaMg ratio greater than 0.95, and an exchangeable sodium content of at least 48%. Liquid limit properties of these clays will exceed 600% which in turn makes them valuable for both the steel and gray iron foundry markets.

It has been demonstrated that industry's own specifications come very close to those recommended in this study. Magcobar Division of Dresser Industries, for example, in response to the first study by Regis (1976) suggested that the cutoff for a unique bentonite should be 70 bbl/ton. They based this figure on the fact that there is variability in sampling and testing procedures (Sloan, 1977), and not on any inherent chemical or physical property. Sloan went on to state that in Dresser's experience a minimum precision of ± 2 cps viscosity is obtained. Dresser also stated that the Fann Viscometer has an accuracy of ± 1.5 cps (3 dial units). Accepting Dresser's value of ± 1.5 cps, this would indicate an accuracy at the 80 bbl/ton reading of ± 5 bbl/ton or a range of 75 to 85 bbl/ton.

Industry has argued that it is possible to blend low grade or low yield bentonites with high yield clays and obtain higher than average values. Studies by Sinclair (1977) at the Bureau of Land Management bentonite testing laboratory at Worland, Wyoming on blending of low and high yield Montana bentonites show that at

best only the theoretical (weighted) average is obtained. In fact, on the majority of the samples, slightly less than the theoretical average was realized. Sinclair's work showed the same results as that by Fulton (1970) of American Colloid. Fulton conducted blending experiments on Wyoming bentonite, blending various proportions of low and high yield bentonites. He too obtained either the theoretical average yields or slightly below average. In addition, Versar (1976, p. 159) reports that when two natural bentonites are blended to meet customer specifications, the yield of the blend is less than the arithmetic average (weighted) of the constituents. The research reported on in this study also indicates that the blending of bentonites with low yields and high water losses is not feasible with bentonite having properties less than those stated previously.

It is further proposed that Western United States bentonite be defined as shown in Figure 12. Throughout the Western states, bentonite occurs as three well defined varieties:

1.	Ca Bentonite:	Na/CaMg ratio <0.1 Exchangeable Na(%) <5% Yield <45 bbl Water Loss >50 ml Water Holding Capacity <150%
2.	Mixed Ca-Na Bentonite: (Intermediate)	Na/CaMg ratio = 0.1-0.9 Exchangeable Na(%) = 5%-48% Yield = 45-75 bbl Water Loss = 18 ml - 50 ml Water Holding Capacity = 150%-600%
3.	Na Bentonite:	Na/CaMg ratio >0.9 Exchangeable Na(%) >48% Yield >75-80 bbl/ton Water Loss <17.0 ml Water Holding Capacity >600%

Most bentonite occurring naturally, in place, with the properties of Na bentonite as defined above will meet all market specifications. Major industrial uses for these three bentonite types are shown in Figure 13.

Western bentonite can be expected to have Na/CaMg ratios which fall within ranges shown in Figure 14 and tabulated in Table 6. This range represents the 95% confidence interval and means that for bentonite of a given yield, 95 out of 100 will have a Na/CaMg ratio within that range. Those ranges in the plateau area of Figure 14 cannot be interpreted to mean that the lower limits would indicate high grade bentonite which is reactive to treatment and/or blending. Instead they only show the statistical limits supporting the 80 bbl yield and less than 17 ml water loss criteria of locatable bentonite. Ample evidence supporting these criteria has been cited throughout this report.

Figure 12. Proposed Nomenclature for Distinguishing Various Kinds of Western Bentonite.

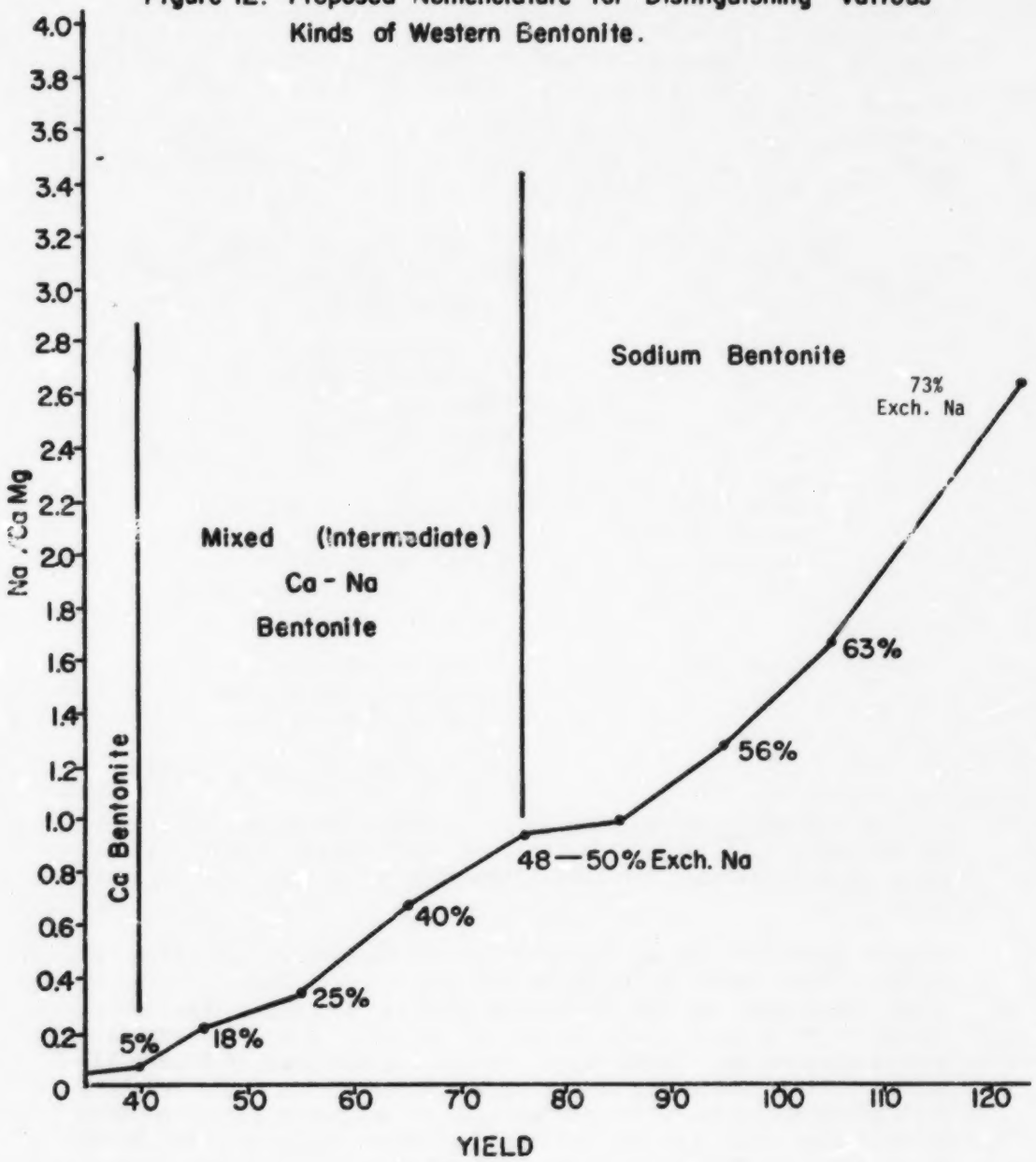


Figure 13. Major Industrial Uses Corresponding to Proposed Bentonite Classification.

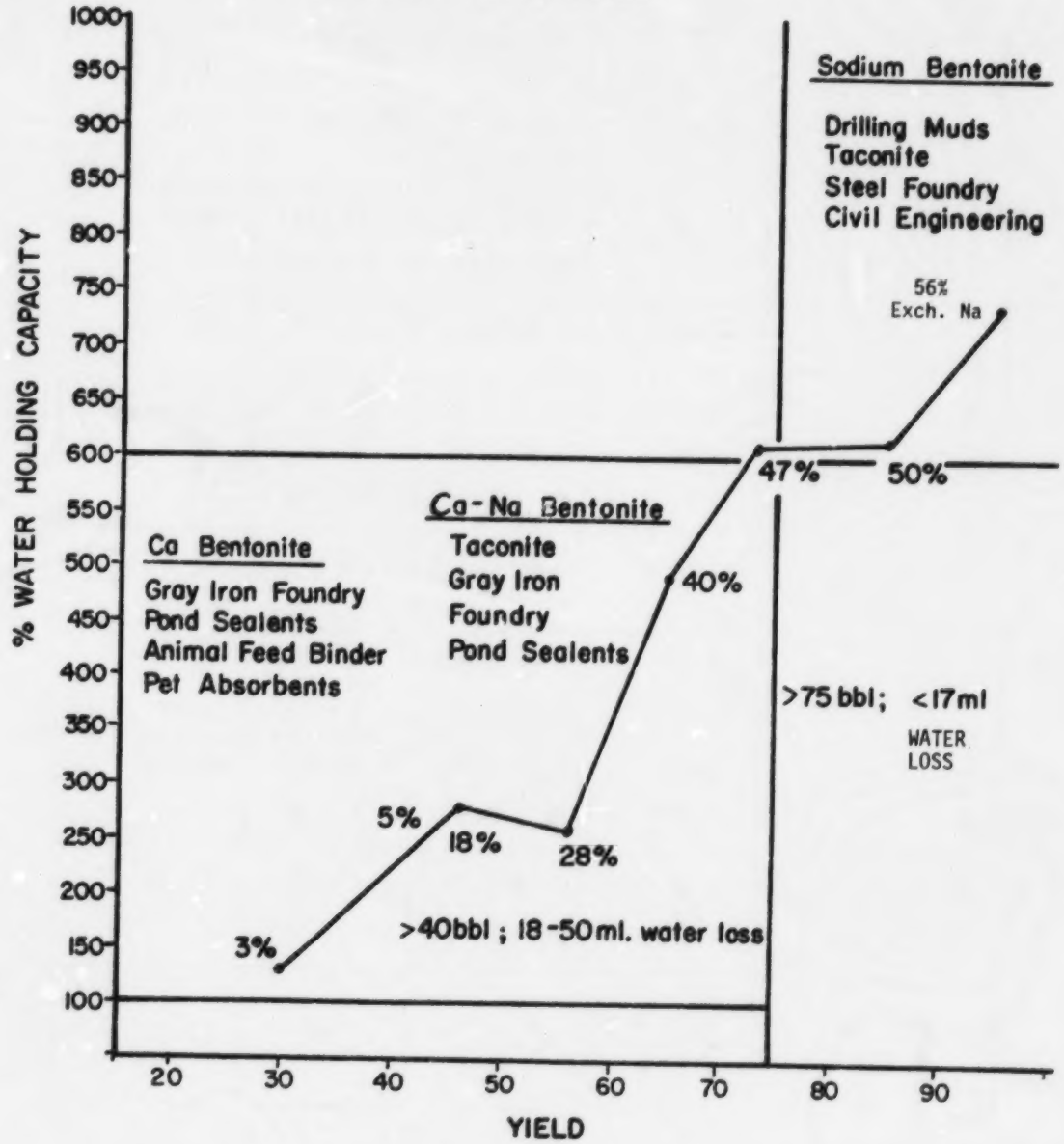


TABLE 6. Tabulation of Ranges at 95% Confidence Level (2σ) for Percent Exchangeable Sodium, Na/CaMg Ratio, Yield and Water Loss.

	% Exch. Na	Na/CaMg Ratio	Yield (bbl)	Water Loss (ml)
SODIUM BENTONITE	65-77	1.84-3.44 $\overline{Mg}$ = 2.64	> 108	< 13
	55-68	1.21-2.11 $\overline{Mg}$ = 1.66	93-112 $\bar{x}$ = 105	< 14
	47-63	0.90-1.66 $\overline{Mg}$ = 1.28	74-105 $\bar{x}$ = 95	< 17.5
	41-56	0.69-1.29 $\overline{Mg}$ = 0.99	65-95 $\bar{x}$ = 85	< 21
PLATEAU RANGE	41-55	0.68-1.20 $\overline{Mg}$ = 0.94	65-95 $\bar{x}$ = 76	< 21
Ca-Na BENTONITES	34-47	0.51-0.88 $\overline{Mg}$ = 0.68	60-72 $\bar{x}$ = 65	< 24
	20-29	0.27-0.41 $\overline{Mg}$ = 0.34	50.66 $\bar{x}$ - 55	< 40
	13-21	0.18-0.26 $\overline{Mg}$ = 0.22	43-50 $\bar{x}$ = 46	< 66
CALCIUM BENTONITE	< 5	< 0.1	< 45	> 50

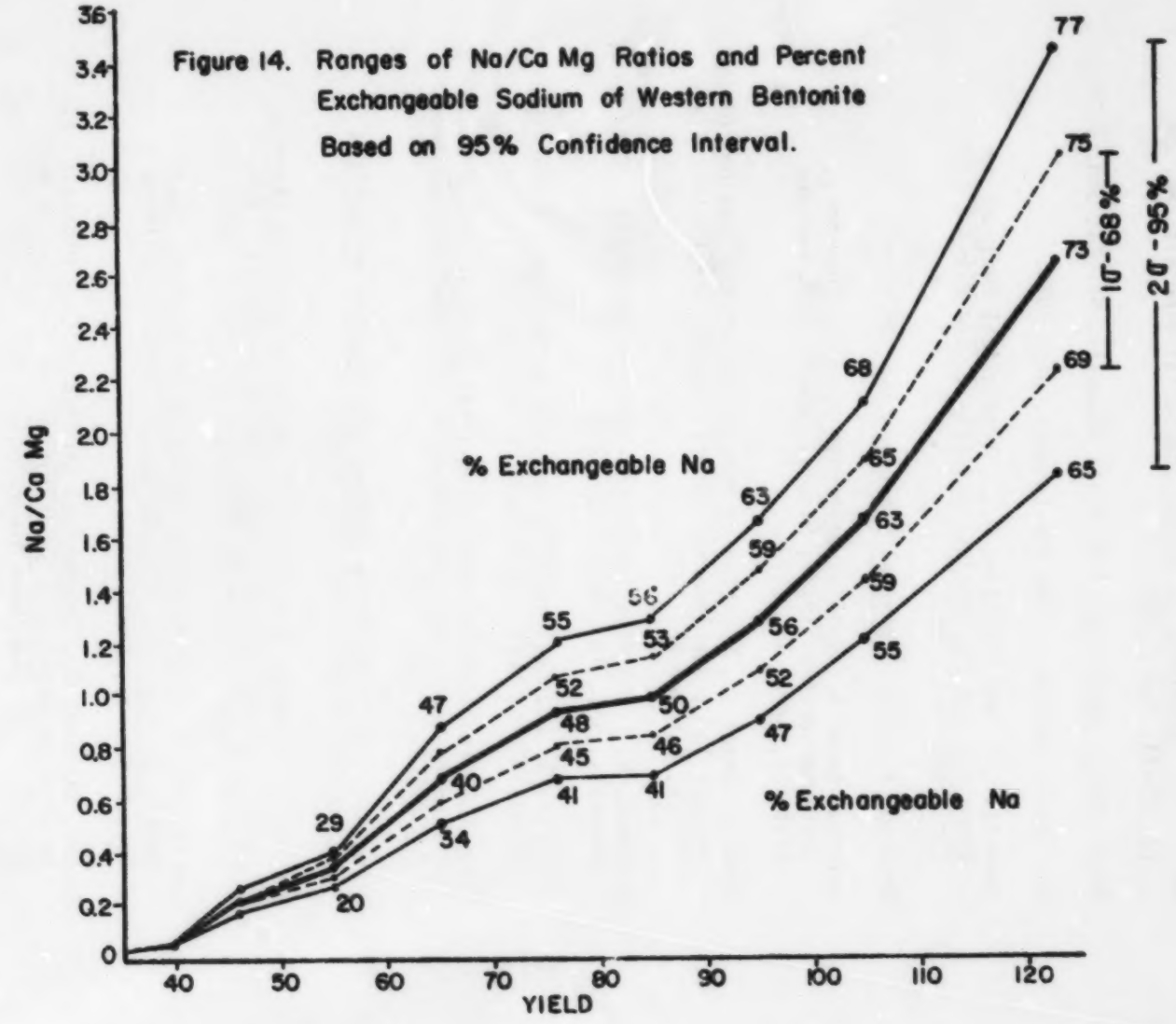


Figure 14. Ranges of Na/Ca Mg Ratios and Percent Exchangeable Sodium of Western Bentonite Based on 95% Confidence Interval.

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